3

INTERACTION OF ATOMS WITH LIGHT

3.1 Two-level system under periodic perturbation (T)

In this problem, we consider a system (e.g., an atom) that has two nondegenerate levels subject to a periodic perturbation that couples these two states. The goal is to describe the temporal evolution of the system, assuming that it is in the lower state initially, and that the lower state does not decay. The upper state decays to some other states with a rate $\Gamma$. This is one of the central problems in atomic and optical physics [in fact, there have been entire books written on the subject, see, for example, Allen and Eberly (1987)] arising in a great variety of situations, as will be discussed in a number of further problems. Note that the content of this problem is closely related to the phenomenon of magnetic resonance (Problem 2.6) and the discussion of the AC Stark and Zeeman shifts in Problem 2.7.

(a) Find differential equations for the time-dependent probability amplitude to be in the upper state, $b(t)$, and the amplitude to be in the lower state, $a(t)$. For the periodic perturbation, assume the form

$$V(t) = V_0 e^{i\omega t},$$

where $V_0$ is real.

Solution

The state of the system is described by the wavefunction

$$|\psi(t)\rangle = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}.$$  

(3.2)

The temporal evolution of the system (neglecting relaxation) can be described by the Schrödinger equation:

$$i \frac{\partial |\psi\rangle}{\partial t} = H |\psi(t)\rangle,$$

(3.3)
where we have set $\hbar = 1$. The Hamiltonian is given by

$$H = \begin{pmatrix} 0 & V(t) \\ V^*(t) & \omega_0 \end{pmatrix},$$  \hspace{1cm} (3.4)

where $\omega_0$ is the separation between the upper and the lower state of the two-level system. The explicit form of (3.3) assuming the Hamiltonian (3.4) and the form of the periodic perturbation (3.1) is:

$$\frac{id}{dt} a = V_0 e^{i\omega t} b(t), \hspace{1cm} (3.5)$$

and

$$\frac{id}{dt} b = V_0 e^{-i\omega t} a(t) + \omega_0 b(t). \hspace{1cm} (3.6)$$

In order to include relaxation, an additional term should be added\(^1\) to the right hand side of equation (3.6):

$$\frac{id}{dt} b = V_0 e^{-i\omega t} a(t) + (\omega_0 - i\Gamma/2) b(t). \hspace{1cm} (3.7)$$

This term ensures that the amplitude $b(t)$ decays at a rate $\Gamma/2$, and the population decays at a rate $\Gamma$.

(b) We now proceed to solve the equations with the initial condition

$$|\psi(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \hspace{1cm} (3.8)$$

Analytical solutions are possible, particularly in a number of limiting cases.

Determine the probability $P(t) = |b(t)|^2$ of finding the system in the upper state under the conditions where $\Delta = \omega - \omega_0 = 0$ and there is no relaxation ($\Gamma = 0$).

One can solve for $a(t)$ and $b(t)$ by using what is known as the interaction picture via a unitary transformation. In the interaction picture, the unperturbed wavefunctions do not change in time. In the present case, this is exactly analogous to the frame rotating with frequency $\omega = \omega_0$ used in the analysis of magnetic resonance, as discussed in Problems 2.6 and 2.7. Such a transformation removes the time dependence in the Hamiltonian $H$ [Eq. (3.4)] and changes the energy

\(^1\) Introducing relaxation in this way is equivalent to using instead of (3.4) a nonHermitian Hamiltonian

$$H = \begin{pmatrix} 0 & V(t) \\ V^*(t) & \omega_0 - i\Gamma/2 \end{pmatrix}.$$  

We warn the reader that while this works in this case (and some others), in general, it is not correct to “write in” relaxation terms into the Hamiltonian, and in the density matrix formalism [see, for example, Appendix G and Stenholm (1984)] a separate “relaxation matrix” is usually introduced.
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separation between the states from $\omega_0$ to $\omega_0 - \omega$. Therefore, in the rotating frame, on resonance the two states are degenerate and the Hamiltonian is given by

$$H^{(\text{rot})} = \begin{pmatrix} 0 & V_0 \\ V_0 & 0 \end{pmatrix}.$$ (3.9)

**Solution**

Of course, this problem is exactly analogous to Problem 2.6, and can be solved by saying that the two-level system is a spin-$\frac{1}{2}$ particle in a static magnetic field $\vec{B}_0$ subjected to a rotating transverse field $\vec{B}_\perp(t)$. Then the oscillations between the two levels correspond to the precession of the magnetic moment about the transverse field in the rotating frame.

Here we offer another method of solution. We can solve for the energy eigenstates of the matrix (3.9) using the same techniques as applied in Problem 1.4, and obtain

$$\left| 1 \right> = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$ (3.10)

$$\left| 2 \right> = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$ (3.11)

These eigenstates correspond to the energy eigenvalues

$$E_1 = -V_0,$$ (3.12)

$$E_2 = V_0.$$ (3.13)

The initial state $\psi(0)$ [Eq. (3.8)] can be written as a superposition of the energy eigenstates $\left| 1 \right>$ and $\left| 2 \right>$:

$$\left| \psi(0) \right> = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} (\left| 1 \right> + \left| 2 \right>) = \frac{1}{2} \left( \begin{pmatrix} 1 \\ -1 \end{pmatrix} + \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right).$$ (3.14)

According to the time-dependent Schrödinger equation (3.3), the energy eigenstates acquire a phase as they evolve in time

$$\left| \psi(t) \right> = \frac{1}{\sqrt{2}} (e^{iV_0 t} \left| 1 \right> + e^{-iV_0 t} \left| 2 \right>) .$$ (3.15)

Since the upper state can also be expressed as a linear superposition of $\left| 1 \right>$ and $\left| 2 \right>$, namely

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (\left| 2 \right> - \left| 1 \right>),$$ (3.16)
the amplitude of finding the system in the upper state is given by

\[
b(t) = \frac{1}{2}(-\langle 1 | + \langle 2 |) (e^{iV_0 t}|1\rangle + e^{-iV_0 t}|2\rangle) = -\frac{1}{2}(e^{iV_0 t} - e^{-iV_0 t}) = -i \sin(V_0 t) .
\]

Therefore the probability \( P(t) \) of finding the system in the upper state under these conditions is given by

\[
P(t) = |b(t)|^2 = \sin^2(V_0 t) .
\]

Figure 3.1 shows the probability of finding the system in the upper state [this plot is obtained by numerically solving the time-dependent Schrödinger equation with the full Hamiltonian (3.7)]. One can see that this probability oscillates between 0 and 1 with a frequency of \( \Omega_R = 2V_0 \). This frequency is called the resonant Rabi frequency.\(^2\)

\(^2\) Note that in the literature one also finds definitions which differ from this one by a numerical factor.
At small times $t$, the probability of finding the system in the upper state increases quadratically with time. This is an interference effect. Consider an infinitesimal time interval $dt$. The quantum mechanical amplitude of finding the system in the upper state scales proportional to $dt$. In another interval of duration $dt$, as long as the upper state is essentially “empty” and stimulated emission back to the lower state can be neglected, there is a similar contribution to the upper state amplitude. The contribution from the two time intervals is thus twice in amplitude, and four times in transition probability compared to a single time interval. The quadratic behavior can be limited (even before a significant population builds up in the upper state) when the contributions to the amplitude from different time intervals are not in phase. This dephasing can occur due to detuning of the perturbation frequency from the resonance as will be considered in part (c) or due to relaxation as in part (e).

(c) Determine the probability $P(t) = |b(t)|^2$ of finding the system in the upper state for $\Gamma = 0$, assuming that $a(t) \approx 1$ throughout [this is the case, for example, when the magnitude of frequency detuning $|\omega - \omega_0|$ greatly exceeds $V_0$].

Solution

We can begin by writing

$$b(t) = \beta(t)e^{-i\omega_0 t}.$$  \hspace{1cm} (3.21)

We choose this form because in the absence of the perturbation, Eq. (3.21) with $\beta(t)$ constant would satisfy the time-dependent Schrödinger equation (3.3). Therefore the entire effect of the perturbation is contained in the time dependence of $\beta$. Substituting expression (3.21) into the differential equation (3.6) yields:

$$\frac{d\beta}{dt}e^{-i\omega_0 t} - i\omega_0 \beta(t)e^{-i\omega_0 t} = -iV_0 e^{-i\omega t}a(t) - i\omega_0 \beta(t)e^{-i\omega_0 t}.$$  \hspace{1cm} (3.22)

Cancelling like terms on either side of Eq. (3.22) leaves us with

$$\frac{d\beta}{dt} = -iV_0 e^{-i\Delta t}a(t).$$  \hspace{1cm} (3.23)

Using the assumption that $a(t) \approx 1$, we integrate to solve for $\beta(t)$:

$$\beta(t) = -iV_0 \int_0^t e^{-i\Delta t'}dt'$$  \hspace{1cm} (3.24)

$$= \frac{V_0}{\Delta} (e^{-i\Delta t} - 1)$$  \hspace{1cm} (3.25)

$$= \frac{V_0}{\Delta} e^{-i\Delta t/2} \left[ \frac{2}{i} \sin \left( \frac{\Delta t}{2} \right) \right].$$  \hspace{1cm} (3.26)
Therefore, from Eqs. (3.21) and (3.26), the probability $P(t)$ of finding the system in the excited state is given by

$$P(t) = |b(t)|^2 = \frac{(2V_0)^2}{\Delta^2} \sin^2 \left( \frac{\Delta t}{2} \right).$$  \hspace{1cm} (3.27)

The probability $P(t)$ to find the system in the upper state is plotted in Fig. 3.2. We have chosen $V_0 = 1$ (since $V_0$ has dimensions of frequency, this means that we have also chosen a particular calibration of the time axis). One can see that this probability (or the upper state population) oscillates between 0 and a small value with a frequency $\Omega_R \approx \Delta$.

(d) Knowing the resonant solution (3.20) and the far-detuned solution (3.27), guess the general solution for $\Gamma = 0$. This solution can also be obtained analytically by solving the system of differential equations [(3.5) and (3.6)] without approximations [see, for example, Ramsey (1985), Chapter V].

**Solution**

Interpolating between Eq. (3.27) and (3.20), the general solution is given by:

$$P(t) = \frac{(2V_0)^2}{(2V_0)^2 + \Delta^2} \sin^2 \left( \frac{1}{2} \left[ (2V_0)^2 + \Delta^2 \right]^{1/2} t \right).$$  \hspace{1cm} (3.28)
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**Fig. 3.3** Same as Fig. 3.1, but with $\Gamma = 0.3$. The Rabi oscillations are damped.

**Fig. 3.4** Same as Figs. 3.1 and 3.3, but with $\Gamma = 10$. The system no longer exhibits oscillatory behavior (overdamped regime). Note the change in the vertical scale.

(e) Next, we explore the effect of relaxation. To visualize various regimes of the system’s behavior, plot the numerical solution of the system of Eqs. (3.5), (3.7) on resonance ($\Delta = 0$) for $\Gamma = 0.3$ and $\Gamma = 10$. (One can use, for example, Mathematica® to find and plot the numerical solutions.)
Solution

Figure 3.3 shows evolution with the same parameters as Fig. 3.1, except now $\Gamma = 0.3$. One observes Rabi oscillations with decreasing amplitude due to the loss of atoms to other states. Such damped oscillations occur for $\Gamma < 2\Omega_R$. For higher values of $\Gamma$, the system is overdamped and oscillation ceases. This is illustrated in Fig. 3.4, where $\Gamma = 10$. (Note the change in the vertical scale in the figure.) In the overdamped regime, at short times, the upper state population grows as if there was no relaxation, but then it “saturates” at a small level

$$P_{\text{max}} \sim \left( \frac{\Omega_R}{\Gamma} \right)^2,$$

and then eventually decays away. The maximum upper state population occurs at a time $t_{\text{max}} \sim 2\pi/\Gamma$.

By solving the coupled differential equations (3.5) and (3.7) [using techniques similar to those employed in the solution of the undamped system (3.5) and (3.6) in part (b) of this problem], one obtains the general analytic formula for the time dependence of the population of the upper state (Demtröder 1996):

$$P(t) = \frac{(2V_0)^2 e^{-\Gamma t/2}}{(2V_0)^2 + \Delta^2 + \Gamma^2/4} \sin^2 \left( \frac{t}{2} \sqrt{\frac{\Delta + \Gamma/2}{2} + (2V_0)^2} \right).$$

(3.30)

3.2 Quantization of the electromagnetic field (T)

In this tutorial, we will briefly review the quantization of the electromagnetic field, which will provide us with some key insights useful in understanding many important phenomena, such as spontaneous emission (Problem 3.3), the noise properties of light fields (Problem 8.8), and the Casimir effect [see, for example, Lamoreaux (1997) and references therein] to name a few. Detailed discussions of this important topic can be found in many texts, for example, Heitler (1954), Sakurai (1967), Shankar (1994), and Loudon (2000).

In the quantization of the electromagnetic field, each mode of the electromagnetic field is put into one-to-one correspondence with a simple harmonic oscillator (SHO). A mode is defined by a wave vector $\vec{k}$ and a polarization $\hat{\epsilon}$, and, for simplicity, we will restrict our considerations in this problem to a single mode. Including all modes involves summing the following results over all possible $\vec{k}$ (hence all possible frequencies $\omega$) and accounting for two orthogonal polarizations.

Consider a light field described by a vector potential $\vec{A}(\vec{r}, t)$ in the Coulomb gauge (in which $\vec{\nabla} \cdot \vec{A} = 0$).\(^3\) We assume no free currents or charges, so the

\(^3\) As we will see in Problem 3.3, the vector potential turns out to be a useful representation for the light field when we consider its interaction with atomic systems.
scalar potential can be set to zero. From Maxwell’s equations one finds that $\vec{A}(\vec{r}, t)$ satisfies the wave equation

$$\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = 0. \quad (3.31)$$

Recall that the electric $\vec{E}(\vec{r}, t)$ and magnetic $\vec{B}(\vec{r}, t)$ fields are related to the vector potential via

$$\vec{E}(\vec{r}, t) = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad (3.32)$$

$$\vec{B}(\vec{r}, t) = \nabla \times \vec{A}. \quad (3.33)$$

To see how the correspondence between a mode of the light field and an SHO is made, we start with the general solution to the wave equation (3.31) for a given mode:

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \left[ C_0 \hat{\epsilon} e^{i(\vec{k}\cdot\vec{r} - \omega t)} + C_0^* \hat{\epsilon}^* e^{-i(\vec{k}\cdot\vec{r} - \omega t)} \right], \quad (3.34)$$

where $\vec{A}$ is normalized with respect to a box of volume $V$ (this box normalization is a technique to deal with the fact that plane waves are nominally of infinite extent and so cannot be normalized unless we restrict the volume over which we integrate). Making the change of notation

$$C(t) = C_0 e^{-i\omega t}, \quad (3.35)$$

we have

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \left[ C(t) \hat{\epsilon} e^{i\vec{k}\cdot\vec{r}} + C^*(t) \hat{\epsilon}^* e^{-i\vec{k}\cdot\vec{r}} \right], \quad (3.36)$$

or

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \left[ C(t) \hat{\epsilon} e^{i\vec{k}\cdot\vec{r}} + \text{c.c.} \right], \quad (3.37)$$

so that all of the time evolution is contained in $C(t)$ (c.c. denotes the complex conjugate).

(a) Show that the total energy $E$ of the light field is given by

$$E = \frac{1}{2\pi} \frac{\omega^2}{c^2} |C(t)|^2. \quad (3.38)$$
Solution

The energy in the light field is given by
\[ E = \frac{1}{8\pi} \int_V (\mathbf{E}^2 + B^2) \, dV, \]
(3.39)
and using Eqs. (3.32) and (3.33) with the expression for the vector potential (3.37) we obtain for the electric and magnetic fields
\[ \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = \frac{\omega}{c\sqrt{V}} \left[ iC(t)\mathbf{e} e^{i\mathbf{k} \cdot \mathbf{r}} + c.c. \right], \]
(3.40)
\[ \mathbf{B} = \nabla \times \mathbf{A} = \frac{1}{\sqrt{V}} \left[ iC(t)(\mathbf{k} \times \mathbf{e}) e^{i\mathbf{k} \cdot \mathbf{r}} + c.c. \right], \]
(3.41)
where we have made use of the fact that, according to the definition (3.35),
\[ \frac{\partial}{\partial t} C(t) = -i\omega C(t). \]
(3.42)
Keeping in mind that \( \mathbf{e} \) is a complex vector, hence
\[ \mathbf{e}^\ast \cdot \mathbf{e} = 1, \]
(3.43)
\[ (\mathbf{k} \times \mathbf{e}^\ast) \cdot (\mathbf{k} \times \mathbf{e}) = k^2 = \frac{\omega^2}{c^2}, \]
(3.44)
after some calculation one finds that quantities \( \propto C(t)^2 \) or \( \propto C^\ast(t)^2 \) cancel when we add the square of the electric field to the square of the magnetic field and there are four terms \( \propto |C(t)|^2 \). Summing these terms and integrating over the volume of the box we obtain Eq. (3.38):
\[ E = \frac{1}{2\pi} \frac{\omega^2}{c^2} |C(t)|^2. \]

(b) Now consider a classical simple harmonic oscillator (SHO), whose Hamiltonian is given by
\[ H_{sho} = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2, \]
(3.45)
where \( q \) is the position and \( p \) is the momentum of the particle with mass \( m \). A standard trick is to rescale \( q \) and \( p \) according to
\[ p = \sqrt{m\omega} P, \]
(3.46)
\[ q = \frac{Q}{\sqrt{m\omega}}, \]
(3.47)
so that
\[ H_{sho} = \frac{\omega}{2} (Q^2 + P^2) \].

(The rescaling gives \( Q \) and \( P \) the same units.)

Assuming \( Q = \alpha_0 \cos \omega t \), compare the time dependence of \( Q \) and \( P \) to the time dependence of the real and imaginary parts of \( C(t) \) [Eq. (3.35)]. Also compare the energy \( E \) in the electromagnetic field from Eq. (3.38) to the Hamiltonian for the SHO.

**Solution**

We begin with the relation between \( q \) and \( p \)
\[ p = m \frac{dq}{dt} , \]
and make the substitutions suggested in (3.46) and (3.47) to obtain
\[ \omega P = \frac{dQ}{dt} . \]

Therefore
\[ Q(t) = \alpha_0 \cos \omega t , \]
\[ P(t) = -\alpha_0 \sin \omega t . \]

This can be compared to the time dependences of the real and imaginary parts of \( C(t) \)
\[ \text{Re}[C(t)] = C_0 \cos \omega t , \]
\[ \text{Im}[C(t)] = -C_0 \sin \omega t . \]

Furthermore, compare the Hamiltonian for the SHO
\[ H_{sho} = \frac{\omega}{2} (Q^2 + P^2) \]
to the energy of the electromagnetic field from Eq. (3.38)
\[ E = \frac{1}{2\pi c^2} \left( |\text{Re}[C(t)]|^2 + |\text{Im}[C(t)]|^2 \right) . \]

This suggests that we can interpret the real and imaginary parts of \( C(t) \) as the \( Q \) and \( P \) variables for a harmonic oscillator. Completing the analogy by saying that
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\[ C(t) \propto Q + iP, \]
and choosing an appropriate constant of proportionality, we have

\[ C(t) = \sqrt{\frac{\pi c^2}{\omega}} \left( Q + iP \right), \quad (3.56) \]

and for the Hamiltonian of any single mode of the free electromagnetic field we have

\[ H_{em} = \frac{\omega}{2} \left( Q^2 + P^2 \right). \quad (3.57) \]

(c) Now that we have linked the electromagnetic field to the SHO, we can apply all
the properties of the quantum mechanical SHO [see, for example, Griffiths (1995)
or Problem 1.2] to a mode of the electromagnetic field. Our first observation is that
the energy eigenstates of the quantum mechanical SHO can be labelled \( |n \rangle \) where
\( n = 0, 1, 2, 3 \ldots \), and they have energies

\[ E_n = \hbar \omega \left( n + \frac{1}{2} \right). \quad (3.58) \]

What is the meaning of the quantum number \( n \) in terms of a mode of the
electromagnetic field?

**Solution**

Each photon carries an energy \( \hbar \omega \), so the number of photons in a mode of the light
field is \( E_n / (\hbar \omega) \). For \( n \gg 1 \), we have \( n \approx E_n / (\hbar \omega) \), so \( n \) corresponds to the number
of photons in the mode. Note that even when there are no photons in the mode,
the mode still has an energy \( \hbar \omega / 2 \). This is the famous zero-point energy. The
existence of the zero-point energy of the electromagnetic field has been demonstrated
in a plethora of quantum electrodynamical effects including, for example, a
recent beautiful experiment by Lamoreaux (1997) measuring what is known as the
Casimir effect [see the review by Milton (2001) and Problem 9.9]. Nonetheless,
the existence of the zero-point energy is mysterious, since if one sums over all possible
modes of the electromagnetic field, an enormous energy density is obtained.
According to general relativity, this energy density would profoundly affect the
evolution of the universe in a manner inconsistent with experimental observations.
Understanding these issues, sometimes called the physics of the vacuum, is among
the most important open issues in modern physics.

(d) As our final exercise, we define the creation and annihilation operators \( a^\dagger \) and
\( a \), respectively (which are analogous to the raising and lowering operators for the
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SHO:

\[
a = \frac{Q + iP}{\sqrt{2\hbar}}, \tag{3.59}
\]

\[
a^\dagger = \frac{Q - iP}{\sqrt{2\hbar}}, \tag{3.60}
\]

where

\[
a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle, \tag{3.61}
\]

\[
a |n\rangle = \sqrt{n} |n-1\rangle, \tag{3.62}
\]

\[
[a, a^\dagger] = 1. \tag{3.63}
\]

One also has

\[
[Q, P] = i\hbar. \tag{3.64}
\]

Write the vector potential (3.37) and the Hamiltonian \(H_{em}\) in terms of the creation and annihilation operators.

**Solution**

According to Eqs. (3.59) and (3.56) we can write

\[
C(t) = \sqrt{\frac{\pi e^2}{\omega}} (Q + iP) = \sqrt{\frac{2\pi\hbar e^2}{\omega}} a. \tag{3.65}
\]

Thus the vector potential in Eq. (3.37) is given by

\[
\vec{A} = \sqrt{\frac{2\pi\hbar e^2}{V\omega}} [a\hat{\epsilon} e^{i\vec{k} \cdot \vec{r}} + a^\dagger \hat{\epsilon}^* e^{-i\vec{k} \cdot \vec{r}}]. \tag{3.66}
\]

We will make use of this form for the vector potential in Problem 3.3.

In order to express \(H_{em}\) in terms of \(a\) and \(a^\dagger\), consider

\[
a^\dagger a = \frac{1}{2\hbar} (Q - iP)(Q + iP) \tag{3.67}
\]

\[
= \frac{1}{2\hbar} (Q^2 - iPQ + iQP + P^2) \tag{3.68}
\]

\[
= \frac{1}{2\hbar} (Q^2 + i[Q, P] + P^2) \tag{3.69}
\]

\[
= \frac{1}{2\hbar} (Q^2 + P^2 - \hbar), \tag{3.70}
\]
which gives us

$$Q^2 + P^2 = \hbar \left( 2a^\dagger a + 1 \right).$$

(3.71)

Employing Eq. (3.71) in (3.57), we obtain

$$H_{em} = \hbar \omega \left( a^\dagger a + \frac{1}{2} \right).$$

(3.72)

Note that according to the solution to part (c) [Eq. (3.58)], the operator $a^\dagger a$ yields the number of photons in the corresponding mode of the electromagnetic field, and for this reason it is generally known as the number operator.

### 3.3 Emission of light by atoms (T)

In this lengthy but important tutorial, we derive the formula for spontaneous and stimulated emission of light by an atomic system in the electric dipole ($E1$) approximation (we will specify exactly what we mean by this approximation somewhat later). The approach taken here is rather formal in contrast to most of the other problems in this book; more intuitive models of atomic transitions are discussed in Problems 2.6 and 3.1. The main reason for this approach is that in order to understand the physical mechanism responsible for spontaneous emission, one must invoke the quantized electromagnetic field (Problem 3.2). This necessitates some level of formal mathematics. In addition, the mathematical tools employed in this tutorial (Fermi’s Golden Rule, the Wigner-Eckart theorem, Clebsch-Gordan coefficients, etc.) are used in many important areas of atomic spectroscopy [see, for example, Sobelman (1992) and Scully and Zubairy (1997)], so it is useful to be acquainted with them.

Let us consider transitions between a ground level $|g\rangle$ with angular momentum $J$ and an excited level $|e\rangle$ with angular momentum $J'$. The Zeeman sublevels are labelled by the projection of the angular momentum along the quantization axis ($z$): $M_J$ and $M'_{J}$, respectively. The energy separation between $|e\rangle$ and $|g\rangle$ is $\hbar \omega_0$.

The first tool we will need is Fermi’s Golden Rule [see, for example, Griffiths (1995) or Bransden and Joachain (1989)], originally obtained by Dirac from first-order time-dependent perturbation theory. According to Fermi’s Golden Rule, the

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4 Since many practicing spectroscopists use the book by Sobelman (1992), we caution the reader that in his notation the initial state of a transition is always labelled $J$ and the final state $J'$. In particular, for emission, this means that the upper state is $J$ and the lower state is $J'$, opposite to our convention.

5 By “first order” we mean that we consider only first-order changes to the wavefunctions induced by the perturbing Hamiltonian $H'$, meaning that the probability to make a transition between the states of interest during the time over which $H'$ acts on the system must be small.
differential transition rate \( dW_{fi} \) from an initial state \( |i\rangle \) to a final state \( |f\rangle \) for atoms subjected to a perturbation described by a Hamiltonian \( H' \) is given by

\[
dW_{fi} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \rho_f(E) P(E) dE ,
\]

where \( \rho_f(E) \) is the *density of states* – the number of states \( |f\rangle \) per unit energy – and \( P(E) \) is the distribution of energies that allow a transition to occur (this will be discussed in more detail below). In the following calculations, we employ the quantized electromagnetic field (Problem 3.2), so \( |i\rangle \) and \( |f\rangle \) include both the atomic state and the photon state. Because there are only a few possible atomic states in the problem we consider, \( \rho_f(E) \) is essentially the density of photon states.

(a) Calculate the density of states function \( \rho_f(E) \) for photons with a given polarization \( \hat{\epsilon} \) and whose wave vectors \( \vec{k} \) are in a differential solid angle \( d\Omega \) (where our coordinate system is centered at the atom; recall that the photons must satisfy \( \hat{\epsilon} \cdot \vec{k} = 0 \)). For the purposes of normalization of the photon wavefunctions, suppose that the photons are contained in a box with volume \( V \) (as in Problem 3.2).

### Solution

The number of photon states \( dN \) in a differential volume of phase space is

\[
dN = \frac{1}{(2\pi)^3} d^3x \frac{d^3p}{\hbar^3} ,
\]

so integrating over the volume of the “box” and making use of the relation \( \vec{p} = \hbar \vec{k} \)

\[
\rho_f(E) = \frac{dN}{dE} = \frac{V}{(2\pi)^3} \frac{E^2}{\hbar^3c^3} d\Omega .
\]

The number of photon states \( dN \) in a differential volume of phase space is

\[
dN = \frac{1}{(2\pi)^3} d^3x \frac{d^3p}{\hbar^3} ,
\]

so integrating over the volume of the “box” and making use of the relation \( \vec{p} = \hbar \vec{k} \)

\[
\rho_f(E) = \frac{dN}{dE} = \frac{V}{(2\pi)^3} \frac{E^2}{\hbar^3c^3} d\Omega .
\]
Equation (3.78) gives the total number of photon states with an energy between \( E \) and \( E + dE \) in a solid angle \( d\Omega \), but we must also include a factor that describes which photon states have the correct frequency so a transition can occur. This function takes into account restrictions on the accessible final states such as energy conservation and momentum conservation. Here we will assume an infinitely heavy nucleus, so we do not have to bother with effects related to atomic recoil. Let us also assume that the only source of line broadening is the finite lifetime \( 1/\gamma \) of the excited state caused by spontaneous emission from \( |e\rangle \rightarrow |g\rangle \) (later we will calculate the spontaneous emission rate \( \gamma \)). We know from the Heisenberg uncertainty relationship that the finite lifetime of the upper state leads to an uncertainty: in particular, the decaying exponential governing the probability to be found in \( |e\rangle \) yields a Lorentzian distribution \( P(\omega) \) of allowed photon frequencies (see Problem 9.3),

\[
P(\omega) = \frac{\gamma/(2\pi)}{(\omega - \omega_0)^2 + (\gamma/2)^2},
\]

where the distribution is normalized so that the integral over all frequencies is unity.

What is the distribution of photon frequencies \( P(\omega) \) that allow a transition to occur in the limit where \( \gamma \) approaches zero? What is the total transition rate integrated over all photon frequencies?

**Solution**

As \( \gamma \rightarrow 0 \), \( P(\omega) \ightarrow \delta(\omega - \omega_0) \), where \( \delta(\omega - \omega_0) \) is the Dirac delta function. To see this, we note three properties of \( P(\omega) \):

- the width of the function \( P(\omega) \) is \( \gamma \), so it tends to zero as \( \gamma \rightarrow 0 \);
- the amplitude of \( P(\omega) \) on resonance \( (\omega = \omega_0) \) is \( 2/(\pi\gamma) \), so it tends to \( \infty \); and
- the integral over \( P(\omega) \) is unity if the range of integration includes \( \omega_0 \) and zero otherwise in the limit \( \gamma \rightarrow 0 \).

This ensures that \( P(\omega) \rightarrow \delta(\omega - \omega_0) \) as \( \gamma \rightarrow 0 \). The result is intuitive since as the linewidth of the transition tends to zero, the only way to induce a transition is to exactly satisfy energy conservation. In this limit, Eq. (3.73) becomes:

\[
dW_{fi} = \frac{2\pi}{\hbar} |\langle f|H'|i \rangle|^2 \rho_f(E) \delta(h\omega_0 - E)dE.
\]
Integrating over photon energies, we obtain the familiar form of Fermi’s Golden Rule:

$$W_{fi} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \rho_f (\hbar \omega_0).$$  \hfill (3.81)

(c) Next we address the matrix element $\langle f | H' | i \rangle$. What is the correct form of the interaction Hamiltonian $H'$? We can begin by writing out the total Hamiltonian for the atomic system in the presence of a light field described by a vector potential $\vec{A}(\vec{r}, t)$ in the Coulomb gauge (see Problem 3.2). For simplicity, we will consider a single-electron atom (extension of the theory to multi-electron atoms is straightforward by taking a sum over all electrons).

The total Hamiltonian for a one-electron atom in the presence of the light field is taken to be

$$H = \frac{1}{2m} \left[ \vec{p} + \frac{e}{c} \vec{A}(\vec{r}, t) \right]^2 - \frac{Ze^2}{r},$$  \hfill (3.82)

where the quantity $\vec{p}$ is the canonical momentum [see, for example, Griffiths (1999) or Landau and Lifshitz (1987) – recall that in this book we define the electron charge to be $-e$].

We break the Hamiltonian into a perturbing Hamiltonian $H'$ and an unperturbed Hamiltonian $H_0$.

Show that

$$H \approx H_0 + H',$$  \hfill (3.83)

where

$$H_0 = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}$$  \hfill (3.84)

is the usual Hamiltonian for an unperturbed one-electron atom and

$$H' = \frac{e}{mc} \vec{p} \cdot \vec{A},$$  \hfill (3.85)

where it is assumed that

$$|\vec{p}| \gg \frac{e}{c} |\vec{A}|.$$  \hfill (3.86)

What is the physical meaning of the condition (3.86)?
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Solution

Simply expanding the first term in the Hamiltonian \( H \) given in Eq. (3.82) yields

\[
\frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 = \frac{\vec{p}^2}{2m} + \frac{e}{2mc} \left( \vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} \right) + \frac{e^2}{2mc^2} \vec{A}^2 .
\] (3.87)

The condition (3.86) allows us to ignore the term \( \propto \vec{A}^2 \), since it is small in comparison to the other terms, so

\[
H \approx \frac{\vec{p}^2}{2m} + \frac{e}{2mc} \left( \vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} \right) - \frac{Ze^2}{r} .
\] (3.88)

Furthermore, the condition (3.86) also permits us to treat the terms involving \( \vec{A} \) as a perturbation, so we say that

\[
H_0 = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}
\]

is our unperturbed Hamiltonian and

\[
H' = \frac{e}{2mc} \left( \vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} \right)
\] (3.89)

is the perturbing Hamiltonian.

Now consider the term

\[
\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} = 2\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} - \vec{p} \cdot \vec{A}
\]
\[
= 2\vec{p} \cdot \vec{A} + \left[ \vec{A}, \vec{p} \right].
\] (3.91)

Recalling that \( \vec{p} \) is the generator of infinitesimal translations [see, for example, Bransden and Joachain (1989)], we have

\[
\left[ \vec{A}, \vec{p} \right] = i\hbar \vec{\nabla} \cdot \vec{A},
\] (3.92)

but since we are using the Coulomb gauge, \( \vec{\nabla} \cdot \vec{A} = 0 \). Using this fact and Eq. (3.91) in (3.89), we obtain the sought after expression (3.85):

\[
H' = \frac{e}{mc} \vec{p} \cdot \vec{A} .
\]

The condition (3.86) merely implies that the forces due to the light field are much smaller than the electrostatic force binding the electron to the nucleus. This can be seen from the following argument. Since the vector potential oscillates with
frequency $\omega$, based on Eq. (3.32) we can estimate that the amplitude of the light electric field $E_0$ is

$$E_0 \sim \frac{1}{c} \frac{\partial A}{\partial t} \sim \frac{\omega}{c} A,$$

so the force acting on the electron due to the light field is

$$F_{\text{light}} \sim eE_0 \sim \frac{e^2}{c} A.$$  

Near resonance, we can say that

$$\omega \approx \omega_0 \sim \frac{e^2}{\hbar a_0}.$$  

If we require that the force $F_{\text{bind}} \sim e^2/a_0^2$ on the electron due to electrostatic attraction to the nucleus is much greater than $F_{\text{light}}$, after a bit of algebra we have the condition

$$\frac{\hbar}{a_0} \gg \frac{e}{c} A.$$  

From the Heisenberg uncertainty relation, we can say that $p \sim \hbar/a_0$, which gives us condition (3.86).

(d) As we have mentioned above, $|i\rangle$ and $|f\rangle$ include both the atomic state and the photon state. In the following we perform calculations for a single mode of the electromagnetic field – later the density of states and distribution functions in Fermi’s Golden Rule will account for the sum over suitable modes. Thus for a complete Hamiltonian which describes both the atom and the light field, we must include the Hamiltonian for the electromagnetic field $H_{\text{em}}$ [Eq. (3.72)], so

$$H_{\text{tot}} = H + H_{\text{em}} = H_0 + H_{\text{em}} + H'.$$

The interpretation of $H_{\text{tot}}$ is straightforward: $H_0$ is the Hamiltonian for the unperturbed atomic system, $H_{\text{em}}$ is the Hamiltonian for the free electromagnetic field, and $H'$ describes the coupling between the two. Ignoring the perturbation $H'$, we see that $H_0$ and $H_{\text{em}}$ act on completely separate systems, so the unperturbed energy eigenstates can be written simply as products of the atomic state and the photon state: $|g, J, M_J, n\rangle$ and $|e, J', M_{J'}, n'\rangle$.

Use the expression (3.66) for the vector potential $\vec{A}$ in terms of creation and annihilation operators in expression (3.85) for $H'$ to obtain matrix elements for emission of a single photon.
Solution

In terms of $a$ and $a^{\dagger}$, we have for $H'$:

$$H' = \frac{e}{m} \sqrt{\frac{2\pi \hbar}{V \omega}} \left[ a(\vec{p} \cdot \hat{\epsilon})e^{i\vec{k} \cdot \vec{r}} + a^{\dagger}(\vec{p} \cdot \hat{\epsilon}^{*})e^{-i\vec{k} \cdot \vec{r}} \right].$$

(3.98)

The initial state is $|i\rangle = |e, J', M'J\rangle |n\rangle$ and the final state is $|f\rangle = |g, J, MJ\rangle |n'\rangle$. Energy conservation [see part (b)] demands that the atom must impart an energy of $\approx \hbar \omega_0$ to the electromagnetic field, so $n' = n + 1$, meaning that this is an emission event. Then only the term with $a^{\dagger}$ in Eq. (3.98) contributes to the matrix element since $\langle n+1|a|n\rangle = 0$, thus

$$\langle f|H'|i \rangle = \frac{e}{m} \sqrt{\frac{2\pi \hbar(n+1)}{V \omega}} \langle g, J, MJ| (\vec{p} \cdot \hat{\epsilon}^{*})e^{-i\vec{k} \cdot \vec{r}}|e, J', M'J\rangle .$$

(3.99)

where we have used

$$\langle n+1|a^{\dagger}|n\rangle = \sqrt{n+1} \langle n+1|n+1\rangle = \sqrt{n+1} .$$

(3.100)

(e) In order to solve for the emission rate, we must now evaluate the matrix elements between the atomic states. It is here that we employ the electric dipole ($E1$) approximation mentioned at the beginning of the problem. We assume that the dimensions of the electron cloud are much smaller than the wavelength of the light, so that

$$\vec{k} \cdot \vec{r} \ll 1 ,$$

(3.101)

and thus $e^{i\vec{k} \cdot \vec{r}} \sim 1$.

Express the atomic matrix element

$$\langle g, J, MJ| \vec{p} \cdot \hat{\epsilon}^{*}|e, J', M'J\rangle$$

in terms of $\vec{r}$ instead of $\vec{p}$.

Solution

We begin by invoking the Heisenberg equation of motion for the atomic variables [see, for example, Bransden and Joachain (1989), Griffiths (1995), or Landau and
Lifshitz (1977)

\[
[\vec{r}, H_0] = i\hbar \frac{d\vec{r}}{dt} = \frac{i\hbar \vec{p}}{m}.
\]

(3.102)

Using (3.102), we can write

\[
\langle g, J, M_f|\hat{\vec{p}} \cdot \hat{\vec{e}}^*|e, J', M_f'\rangle = \frac{m}{i\hbar} \langle g, J, M_f|(\vec{r}H_0 - H_0\vec{r}) \cdot \hat{\vec{e}}^*|e, J', M_f'\rangle
\]

(3.103)

\[
= -im\omega_0 \langle g, J, M_f|\vec{r} \cdot \hat{\vec{e}}^*|e, J', M_f'\rangle.
\]

(3.104)

(f) Introducing the dipole operator \( \vec{d} = -e\vec{r} \), use the spherical basis and the Wigner-Eckart theorem (Appendix F) to express the transition rate for a single mode in terms of Clebsch-Gordan coefficients and the reduced matrix element \( \langle g, J||d||e, J'\rangle \).

Solution

In the spherical basis [see Eq. (F.30)], we have

\[
\vec{d} \cdot \hat{\vec{e}}^* = \sum_q d_q \epsilon_q.
\]

(3.105)

We can employ the electric dipole approximation and Eqs. (3.99) and (3.105) in (3.121) to obtain

\[
\langle f|H'|i\rangle = i\sqrt{\frac{2\pi\hbar\omega_0(n+1)}{V}} \sum_q \langle g, J, M_J|d_q \epsilon_q|e, J', M_J'\rangle.
\]

(3.106)

From the Wigner-Eckart theorem (F.1) we obtain

\[
\langle f|H'|i\rangle = i\sqrt{\frac{2\pi\hbar\omega_0(n+1)}{V}} \frac{\langle g, J||d||e, J'\rangle}{\sqrt{2J+1}} \sum_q \langle J', M_J', 1, q|J, M_J\rangle \epsilon_q.
\]

(3.107)

Taking the absolute value squared of the matrix element yields

\[
|\langle f|H'|i\rangle|^2 = \frac{2\pi\hbar\omega_0(n+1)}{V} \frac{|\langle g, J||d||e, J'\rangle|^2}{2J+1} \left( \sum_q \langle J', M_J', 1, q|J, M_J\rangle \epsilon_q \right)^2
\]

(3.108)

Inserting Eqs. (3.108) and (3.78) into Fermi’s Golden Rule (3.81), and taking \( \omega = \omega_0 \) everywhere yields the formula for stimulated and spontaneous emission into a
single mode

\[ dW_{ge} = \frac{1}{2\pi} \frac{\omega_0^3}{\hbar c^3} (n + 1) \left| \langle g, J | d | e, J' \rangle \right|^2 \left( \sum_q \langle J', M'_j, 1, q | J, M_j \epsilon_q \rangle \right)^2 d\Omega. \]

Here the term 1 in the factor \((n + 1)\) represents spontaneous emission while \(n\) represents stimulated emission.

\((g)\) Calculate the rate of spontaneous emission in any direction with any polarization, assuming the excited state is unpolarized. This is the spontaneous decay rate \(\gamma\) mentioned in part (b).

**Solution**

Let us consider a particular polarization \(\hat{\epsilon}\) for the spontaneously emitted light. There are two independent polarizations for a given \(\vec{k}\), so we will multiply our final result by 2 (since we assume a completely unpolarized sample, there is no preferential direction in space). Without loss of generality, we will choose \(\hat{\epsilon}\) along the quantization axis (\(\hat{z}\)), so \(\epsilon_0 = 1\) and \(\epsilon_{\pm 1} = 0\). Spontaneous emission is induced by vacuum fluctuations, i.e., the zero-point energy, so \(n = 0\). Since all directions of space are equivalent in our problem, we must also sum over the possible ground state Zeeman sublevels (\(M\)) and average over the excited state sublevels (\(M'\)).

Employing these arguments, we obtain from Eq. (3.109):

\[ dW_{ge}^{(spont)} = \frac{1}{2\pi} \frac{\omega_0^3}{\hbar c^3} (2J + 1)(2J' + 1) \sum_{M_j} \sum_{M'_j} \langle J', M'_j, 1, 0 | J, M_j \rangle^2 d\Omega. \]

(3.110)

Now we wish to evaluate the sum over the Clebsch-Gordan coefficients. According to the identity (true so long as \(|j_1 - j_2| \leq j \leq j_1 + j_2\))

\[ \sum_{m_1} \sum_{m_2} \langle j_1, m_1, j_2, m_2 | j, m \rangle^2 = 1. \]

(3.111)

6 This procedure is equivalent to calculating the decay rate for all three possible light polarizations from a given sublevel.

7 This formula comes from the fact that we can project the state vector \(|j, m\rangle\) onto the product basis \(|j_1, m_1\rangle|j_2, m_2\rangle\). Since \(\langle j, m | j, m \rangle = 1\), the sum of the squares of all the coefficients in the expansion must be equal to unity, yielding Eq. (3.111).
Using this identity (3.111), we write
\[
\sum_q \sum_{M_J} \sum_{M'_J} \langle J', M'_J, 1, q | J, M_J \rangle^2 = \sum_{M_J} \left( \sum_{M'_J} \sum_q \langle J', M'_J, 1, q | J, M_J \rangle^2 \right) = \sum_{M_J} 1 = 2J + 1.
\]
(3.112)

The sum with one particular \(q\) should give a third of the total result, since isotropy of space demands that the contributions for different choices of \(q\) are the same, so we conclude that
\[
\sum_{M_J} \sum_{M'_J} ||\langle J', M'_J, 1, 0 | J, M_J \rangle||^2 = \frac{2J + 1}{3},
\]
(3.113)

thus
\[
dW^{(spont)}_{ge} = \frac{1}{6\pi} \frac{\omega_0^3}{\hbar c^3} \frac{|\langle g, J || d || e, J' \rangle|^2}{2J' + 1}.
\]
(3.114)

Integrating over the solid angle and multiplying by 2 for the possible polarizations, we obtain
\[
\gamma = \frac{4\omega_0^3}{3\hbar c^3} \frac{|\langle g, J || d || e, J' \rangle|^2}{2J' + 1}.
\]
(3.115)

Here we have assumed that the state \(|e\rangle\) decays only to \(|g\rangle\), so that the considered transition is solely responsible for the spontaneous emission. If, as is often the case in real atomic systems, the state \(|e\rangle\) can decay to several different states \(|g_i\rangle\), we have
\[
\gamma = \sum_i \gamma_i = \sum_i \xi_i \gamma,
\]
(3.116)

where \(\gamma_i\) are the partial widths and the coefficients \(\xi_i\) are known as the branching ratios. Therefore, in order to determine the magnitude of the reduced matrix element \(|\langle g_i, J || d || e, J' \rangle|^2\) between two particular states from experimentally measurable parameters, one must know both the lifetime \(1/\gamma\) and the branching ratio \(\xi_i\):
\[
|\langle g_i, J || d || e, J' \rangle|^2 = \frac{3\hbar c^3}{4\omega_0^3}(2J' + 1)\xi_i \gamma.
\]
(3.117)
3.4 Absorption of light by atoms

Here we use the tools developed in Problem 3.3 for emission of light to address the inverse process: stimulated absorption of a photon by an atomic system. (The results of this calculation can be compared to those obtained in Problem 3.1 by a different approach.)

We consider the same system as in Problem 3.3: an atom with a ground level \( |g\rangle \) having zero energy and total angular momentum \( J \), and an excited level \( |e\rangle \) with energy \( \hbar \omega_0 \) having angular momentum \( J' \). The Zeeman sublevels are labelled by the projection of the angular momentum along the quantization axis (\( z \)): \( M_J \) and \( M'_{J'} \), respectively.

Suppose a monochromatic light beam (bandwidth of light much narrower than the upper state width, \( \gamma \), equal to the spontaneous emission rate) is incident on an atom in a particular Zeeman sublevel of the ground state. Assume the light is on resonance \( \omega = \omega_0 \) and it is linearly polarized along the quantization axis \( z \), and that the intensity is sufficiently small that the condition

\[
|\vec{p}| \gg \frac{e}{c}|\vec{A}|
\]

still holds.

To find the stimulated absorption rate, we again rely on Fermi’s Golden Rule (3.73):

\[
dW_{fi} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \rho_f(E)P(E)dE,
\]

but now, instead of the density of photon states from Eq. (3.78), we have a single final state (one photon absorbed from a single mode and the atom in a particular Zeeman sublevel of the upper state), thus \( \rho_f = \delta(h\omega - h\omega_0) \).

(a) Use the Hamiltonian (3.98) and the electric dipole approximation to write an expression for the square of the matrix element \( \langle f | H' | i \rangle \), where for stimulated absorption

\[
|i\rangle = |g, J, M_J\rangle|n\rangle
\]

and

\[
|f\rangle = |e, J', M'_{J'}\rangle|n - 1\rangle.
\]

(b) Use the Lorentzian distribution function (3.79) on resonance \( \omega = \omega_0 \) in Fermi’s Golden Rule to write the stimulated absorption rate in terms of the light electric field amplitude \( \mathcal{E}_0 \).

(c) Show that the absorption rate for the \( |g, J, M_J\rangle \rightarrow |e, J', M'_{J'}\rangle \) transition is equal to the rate of stimulated emission for the \( |e, J', M'_{J'}\rangle \rightarrow |g, J, M_J\rangle \) transition.
Hint

In part (c), it may be helpful to employ the relationship between reduced matrix elements (Sobelman 1992),

$$\langle e, J' || d || g, J \rangle = (-1)^{J' - J} \langle g, J || d || e, J' \rangle^* ,$$  \hspace{1cm} (3.118)

and the relationship between Clebsch-Gordan coefficients (Varshalovich et al. 1988),

$$\langle J, M_J, \kappa, q | J', M_J' \rangle = (-1)^{J - J' + q} \sqrt{\frac{2J' + 1}{2J + 1}} \langle J', M_J', \kappa, -q | J, M_J \rangle .$$  \hspace{1cm} (3.119)

Solution

(a) The perturbing Hamiltonian in the electric dipole approximation can be found using Eq. (3.98) and condition (3.101) to be

$$H' = \frac{e}{m} \sqrt{\frac{2\pi \hbar}{V \omega}} \left[ a(\vec{p} \cdot \hat{e}) + a^\dagger(\vec{p} \cdot \hat{e}^*) \right] .$$  \hspace{1cm} (3.120)

Only the term with $a$ in Eq. (3.98) contributes to the matrix element since $\langle n - 1 | a | n \rangle = 0$, thus

$$\langle f | H' | i \rangle = \frac{e}{m} \sqrt{\frac{2\pi \hbar n}{V \omega}} \langle e, J', M_J' | (\vec{p} \cdot \hat{e}) | g, J, M_J \rangle ,$$  \hspace{1cm} (3.121)

where we have used

$$\langle n - 1 | a | n \rangle = \sqrt{n} (n - 1 | n - 1) = \sqrt{n} .$$  \hspace{1cm} (3.122)

The matrix element $\langle e, J', M_J' | (\vec{p} \cdot \hat{e}) | g, J, M_J \rangle$ is given by the complex conjugate of (3.104), so in the spherical basis we obtain:

$$\langle f | H' | i \rangle = -i \sqrt{\frac{2\pi \hbar \omega_0 n}{V}} \sum_q (-1)^q \langle e, J', M_J' | d_q e_{-q} | g, J, M_J \rangle .$$  \hspace{1cm} (3.123)

---

8 Considering the usual phase convention for the spherical harmonics ($Y_m^\ell$'s), the reduced matrix elements for induced electric dipole moments are real, so Eq. (3.118) turns out to be:

$$\langle e, J' || d || g, J \rangle = (-1)^{J' - J} \langle g, J || d || e, J' \rangle .$$
From the Wigner-Eckart theorem (F.1) we obtain
\[
\langle f | H' | i \rangle = -i \sqrt{\frac{2 \pi \hbar \omega_0 n}{V}} \frac{|\langle e, J' || d || g, J \rangle|^2}{\sqrt{2 J' + 1}} \sum_q \langle J, M_J, 1, q | J', M'_J \rangle (-1)^q \epsilon_{-q} .
\] (3.124)

For the case of z-polarized light, \( q = 0 \) (\( \epsilon_0 = 1, \epsilon_{\pm 1} = 0 \)), therefore
\[
\langle f | H' | i \rangle = -i \sqrt{\frac{2 \pi \hbar \omega_0 n}{V}} \frac{|\langle e, J' || d || g, J \rangle|^2}{\sqrt{2 J' + 1}} \langle J, M_J, 1, 0 | J', M'_J \rangle .
\] (3.125)

Squaring the matrix element yields
\[
|\langle f | H' | i \rangle|^2 = \frac{2 \pi \hbar \omega_0 n}{V} \frac{|\langle e, J' || d || g, J \rangle|^2}{2 J' + 1} \langle J, M_J, 1, 0 | J', M'_J \rangle^2 .
\] (3.126)

(b) The absorption rate for photons from a single mode of the electromagnetic field is given by substituting for \( \int P(E) \rho_f(E) dE \) the resonant value of the Lorentzian distribution [Eq. (3.79)], \( 2/(\hbar \pi \gamma) \), into Fermi’s Golden Rule (3.73):
\[
W_{eg} = \frac{4}{\gamma \hbar^2} |\langle f | H' | i \rangle|^2 ,
\] (3.127)

where the square of the matrix element is given by Eq. (3.126).

All that is left to do is relate the number of photons in the mode \( n \) to the electric field amplitude \( E_0 \). The average light intensity \( I \) is given both by the time averaged magnitude of the Poynting vector
\[
I = \frac{c E_0^2}{8 \pi} ,
\] (3.128)

and the product of the photon flux \( n c/V \) and energy per photon \( \hbar \omega \)
\[
I = \frac{n}{V} \hbar \omega c .
\] (3.129)

Equating the two expressions for light intensity \( I \) gives
\[
n = \frac{V E_0^2}{8 \pi \hbar \omega} .
\] (3.130)

Thus the square of the matrix element (3.126) in terms of \( E_0 \) is
\[
|\langle f | H' | i \rangle|^2 = \frac{|\langle e, J' || d || g, J \rangle|^2 E_0^2}{4} \frac{\langle J, M_J, 1, 0 | J', M'_J \rangle^2}{2 J' + 1} ,
\] (3.131)
yielding for the rate of absorption

$$W_{eg} = \frac{1}{\gamma} \frac{|\langle e, J'|d||g, J\rangle|^2 \mathcal{E}_0^2 \langle J, M_J, 1, 0|J', M_{J'}\rangle|^2}{2J' + 1}.$$  \hfill (3.132)

(c) Under the considered conditions, from Eq. (3.109), we have for the absolute value squared of the matrix element describing stimulated emission

$$|\langle g, J, M_J|H'|e, J', M_{J'}\rangle|^2 = \frac{2\pi \hbar \omega \mathcal{V} |\langle g, J||d||e, J'\rangle|^2}{2J' + 1} \langle J', M_{J'}, 1, 0|J, M_J\rangle^2.$$  \hfill (3.133)

Equation (3.130) can be used to express the number of photons in the mode, \(n\), in terms of the electric field amplitude \(\mathcal{E}_0\), and, as discussed in part (b),

$$\int P(E) \rho_f(E) dE = \frac{2}{\hbar \pi \gamma}.$$  \hfill (3.134)

Thus we have for the rate of stimulated emission

$$W_{ge} = \frac{1}{\gamma} \frac{|\langle e, J'|d||g, J\rangle|^2 \mathcal{E}_0^2 \langle J, M_J, 1, 0|J', M_{J'}\rangle|^2}{2J' + 1}.$$  \hfill (3.135)

The final step is to use the relations given in the hint for the problem, Eqs. (3.118) and (3.119) in Eq. (3.135), which gives us:

$$W_{ge} = \frac{1}{\gamma} \frac{|\langle e, J'|d||g, J\rangle|^2 \mathcal{E}_0^2 \langle J, M_J, 1, 0|J', M_{J'}\rangle|^2}{2J' + 1},$$  \hfill (3.136)

so indeed \(W_{ge} = W_{eg}\). It is interesting to compare this argument with that given by Einstein to derive the \(A\) and \(B\) coefficients [see, for example, Griffiths (1995)].

3.5 Resonant absorption cross-section

A very convenient concept when studying the absorption of light by an atomic medium is the absorption cross-section \(\sigma_{abs}\), where the excitation rate is given by the photon flux \(\Phi\) times \(\sigma_{abs}\).

Consider transitions between a ground level \(|g\rangle\) with total angular momentum \(J\) and an excited level \(|e\rangle\) with angular momentum \(J'\), separated in energy by \(\hbar \omega_0\). Assume the atoms are initially unpolarized, and that the incident light is on resonance \((\omega = \omega_0)\). Calculate the absorption cross-section (averaged over the initial sublevels \(M_J\)) assuming only homogeneous Lorentzian broadening of the transition.
Solution

The resonant absorption cross-section $\sigma_{\text{abs}}$ is given by

$$\sigma_{\text{abs}} = \frac{W_{eg}}{\Phi},$$

(3.137)

where $W_{eg}$ is the excitation rate of atoms due to stimulated absorption. We can calculate $W_{eg}$ using Eq. (3.132) from Problem 3.4, where here we choose linear polarization (but, as one can verify, the choice of polarization does not matter for the final result!):

$$W_{eg} = \frac{1}{\gamma_{\text{tot}}} \frac{|\langle g, J||d||e, J'\rangle|^2 e_0^2}{\hbar^2} \sum_{M_J} \sum_{M'_J} \frac{1}{(2J' + 1)(2J + 1)} |\langle J, M_J, 1, 0|J', M'_J \rangle|^2,$$

(3.138)

where $\gamma_{\text{tot}}$ denotes the total width of the transition (including, for example, spontaneous decay to other levels, pressure broadening, etc.) and in order to account for all possible transitions between different Zeeman sublevels, we have summed over the final states ($M'_J$) and averaged over the initial states ($M_J$). We use the formula (3.113) to write

$$\sum_{M_J} \sum_{M'_J} |\langle J, M_J, 1, 0|J', M'_J \rangle|^2 = \frac{2J' + 1}{3},$$

(3.139)

yielding

$$W_{eg} = \frac{1}{\gamma_{\text{tot}}} \frac{|\langle g, J||d||e, J'\rangle|^2 e_0^2}{\hbar^2} \frac{1}{3(2J + 1)}.$$

(3.140)

The photon flux is given by

$$\Phi = \frac{1}{\hbar \omega_0} \frac{c e_0^2}{8 \pi},$$

(3.141)

so we have

$$\sigma_{\text{abs}} = \frac{8\pi \omega_0}{3} \frac{1}{c} \frac{\gamma_{\text{tot}}}{\hbar} \frac{|\langle g, J||d||e, J'\rangle|^2}{2J + 1}.$$

(3.142)

Next we can express the reduced dipole moment $|\langle g, J||d||e, J'\rangle|$ in terms of the spontaneous decay rate between $|e\rangle$ and $|g\rangle$ [Eq. (3.115)], known as the partial...
width $\gamma_p$:

$$|\langle g, J || d || e, J' \rangle|^2 = \left(2J' + 1\right) \frac{3\hbar c}{4\omega_0^3} \gamma_p, \quad (3.143)$$

which when substituted into Eq. (3.142) gives us

$$\sigma_{abs} = \frac{2\pi c^2}{\omega_0^2} \frac{2J' + 1}{2J + 1} \frac{\gamma_p}{\gamma_{tot}}, \quad (3.144)$$

or

$$\sigma_{abs} = \frac{\lambda^2}{2\pi} \frac{2J' + 1}{2J + 1} \frac{\gamma_p}{\gamma_{tot}}, \quad (3.145)$$

where $\lambda$ is the wavelength of the transition. The factors $2J + 1$ and $2J' + 1$ are the statistical weights of the ground and excited states, respectively.

This is a very interesting and important result. Take, for example, a closed ($\gamma_p = \gamma_{tot}$) $J \rightarrow J$ transition:

$$\sigma_{abs} = \frac{\lambda^2}{2\pi}, \quad (3.146)$$

which does not depend on anything except the wavelength of the light! Thus the resonant absorption cross-section $\sigma_{abs}$ is the same for both weak and strong transitions. The common notion that weak transitions have small absorption cross sections comes from the $\gamma_p/\gamma_{tot}$ factor. Also note that, in fact, the same formula, Eq. (3.145), holds for magnetic dipole transitions ($M1$), electric quadrupole ($E2$), etc.

### 3.6 Absorption cross-section for a Doppler-broadened line

In dilute thermal atomic vapors, the dominant line broadening mechanism for optical transitions is related to Doppler shifts of the light “seen” by moving atoms. Suppose we consider fluorescence in the $\hat{z}$-direction. For an atom moving with velocity $v_z$ along $\hat{z}$, the observed frequency of the emitted light is

$$\omega' \approx \omega \left(1 + \frac{v_z}{c}\right), \quad (3.147)$$

The atoms in a vapor cell follow a Maxwellian velocity distribution, i.e., the density of atoms $n_v(v_z)dv_z$ with a velocity component along $z$ between $v_z$ and
\[ v_z + dv_z \text{ is} \]

\[ n_v(v_z)dv_z = n_{\text{tot}} \sqrt{\frac{M}{2\pi k_B T}} e^{-Mv_z^2/(2k_BT)} dv_z, \quad (3.148) \]

where \( n_{\text{tot}} \) is the total density of atoms, \( M \) is the mass of the atom, and \( k_B \) is Boltzmann’s constant. When Doppler broadening dominates the width of the transition, this leads to a Gaussian distribution in the fluorescence spectrum:

\[ I_F(\Delta) = I_F(0)e^{-\left(\frac{\Delta}{\Gamma_D}\right)^2}, \quad (3.149) \]

where \( I_F(\Delta) \) is the fluorescence intensity, \( \Delta = \omega - \omega_0 \) is the detuning of the light frequency \( \omega \) from the resonance frequency \( \omega_0 \), and

\[ \Gamma_D = \frac{\omega_0 c}{M} \sqrt{\frac{2k_BT}{M}} \quad (3.150) \]

is the Doppler width.

Suppose the peak resonant light absorption cross-section for stationary atoms is \( \sigma_0 \) (see Problem 3.5) and the homogeneous width of the transition (FWHM) is \( \gamma \). What is the peak absorption cross-section \( (\sigma_D) \) if atoms are in thermal motion so the Doppler width is large: \( \Gamma_D \gg \gamma \)?

**Solution**

In the absence of Doppler broadening, the homogeneous (Lorentzian) absorption profile is:

\[ \sigma_{\text{hom}}(\Delta) = \sigma_0 \frac{\gamma^2/4}{\Delta^2 + \gamma^2/4}, \quad (3.151) \]

where \( \Delta = \omega - \omega_0 \) is the detuning of the light frequency \( \omega \) from the resonance frequency \( \omega_0 \).

In the limit of large Doppler width, the frequency-dependent cross-section is written in the form

\[ \sigma(\Delta) = \sigma_D e^{-\left(\frac{\Delta}{\Gamma_D}\right)^2}. \quad (3.152) \]

In order to relate \( \sigma_D \) and \( \sigma_0 \), we notice that Doppler broadening does not change the area under the absorption curve. Indeed, inhomogeneous broadening (i.e., broadening arising due to a difference in resonance frequencies for different atoms) just spreads the center frequencies of resonances for individual atoms...
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without affecting the shape of the absorption profile for each atom. We have:

\[
\int_{-\infty}^{\infty} \sigma_{\text{hom}}(\Delta) d\Delta = \frac{\pi}{2} \gamma \sigma_0 ; \tag{3.153}
\]

\[
\int_{-\infty}^{\infty} \sigma_D(\Delta) d\Delta = \sqrt{\pi} \Gamma_D \sigma_D . \tag{3.154}
\]

Setting these two integrals equal to each other we obtain:

\[
\sigma_D = \frac{\sqrt{\pi}}{2} \frac{\gamma}{\Gamma_D} \sigma_0 \approx 0.89 \times \frac{\gamma}{\Gamma_D} \sigma_0 . \tag{3.155}
\]

3.7 Saturation parameters (T)

Consider an ensemble of atoms that are illuminated by a light field. Suppose we want to measure some property of the atoms with the light – for example, we are interested in determining the strength of a particular transition. In this situation, we need to be careful that the light field itself does not perturb the property of the atoms we are trying to measure. On the other hand, perhaps we are interested in observing some nonlinear optical process or maybe we want to optically pump all of the atoms into a particular Zeeman sublevel. In these cases, it is necessary that the light field strongly perturb the atomic system.

The crucial parameter that characterizes what regime we are in – whether or not the light field strongly perturbs the populations of the atomic states – is called the *saturation parameter* \( \kappa \). The general form of the saturation parameter is

\[
\kappa = \frac{\text{excitation rate}}{\text{relaxation rate}} . \tag{3.156}
\]

The tricky part is that the exact form of \( \kappa \) and the behavior of the system as a function of \( \kappa \) depend on the specific system under consideration – the atomic level structure, the relaxation mechanisms, etc. In this problem, we consider a variety of systems in order to gain familiarity with calculating saturation parameters and understanding their implications.

In the following cases (a) and (b), assume that the light is tuned to resonance and that the optical depth is small, i.e.

\[
n \sigma_{\text{abs}} \ell \ll 1 , \tag{3.157}
\]

where \( \ell \) is the length of the atomic sample, \( n \) is the atomic number density, and \( \sigma_{\text{abs}} \) is the appropriate absorption cross-section (see Problems 3.5 and 3.6). The quantity \( \ell_0 = (n \sigma_{\text{abs}})^{-1} \) is commonly referred to as the absorption length. The
condition (3.157) ensures that the intensity of the light field does not significantly change as the light propagates through the sample and, as long as all dimensions of the atomic sample are similarly small, that high atomic density effects such as radiation trapping\(^9\) are not important. Additionally we assume that the average spacing between the atoms \(n^{-1/3}\) is considerably larger than the wavelength of the light \(\lambda\). This allows us to ignore effects that involve cooperative behavior of the atoms [such as Dicke superradiance (Dicke 1954), see Problem 3.14].

(a) Consider two-level stationary atoms for which the only source of line broadening is the spontaneous decay of the upper state \(|e\rangle\) back to the lower state \(|g\rangle\) (Fig. 3.5). Calculate the saturation parameter \(\kappa\) for the \(|g\rangle \rightarrow |e\rangle\) transition for narrow-band (monochromatic) incident light, and find the dependence of the fluorescence intensity on \(\kappa\).

**Solution**

The excitation rate \(\Gamma_{\text{pump}}\) (we can think of the light effectively “pumping” the atoms into the excited state) is given by Eq. (3.132) from Problem 3.4:

\[
\Gamma_{\text{pump}} = \frac{d^2 E_0^2}{\gamma_0},
\]

(3.158)

where \(d\) is the dipole matrix element \(\langle e|d|g\rangle\) between the states, \(E_0\) is the amplitude of the light electric field, \(\gamma_0\) is the spontaneous decay rate of \(|e\rangle\) to \(|g\rangle\), and we have

\(^9\) If the atomic density is sufficiently high, there can be a significant probability that spontaneously emitted photons are re-absorbed. Thus the photons must diffuse out of the atomic sample, which affects, for example, measurements of excited state lifetimes. See, for example, Corney (1988).
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set $\hbar = 1$. The relaxation rate in this problem is $\gamma_0$, so from (3.156) we have

$$\kappa = \frac{\Gamma_{\text{pump}}}{\gamma_0} = \frac{d_0^2e_0^2}{\gamma_0^2}. \tag{3.159}$$

The fluorescence intensity $I_F$ is proportional to the number of atoms in the excited state $N_e$ multiplied by the spontaneous decay rate $\gamma_0$. To find the population of the upper state we can write rate equations for the number of atoms in the excited state $N_e$ and the number of atoms in the ground state $N_g$:

$$\frac{dN_g}{dt} = -\Gamma_{\text{pump}}N_g + (\gamma_0 + \Gamma_{\text{pump}})N_e, \tag{3.160}$$

$$\frac{dN_e}{dt} = +\Gamma_{\text{pump}}N_g - (\gamma_0 + \Gamma_{\text{pump}})N_e. \tag{3.161}$$

We also know that $N_e + N_g = N_{\text{tot}}$ where $N_{\text{tot}}$ is the total number of atoms in the sample. We have included the pumping rate for both the $|g\rangle \rightarrow |e\rangle$ transition and the $|e\rangle \rightarrow |g\rangle$ transition because at sufficiently high light powers ($\kappa \gtrsim 1$), stimulated emission from the upper state becomes important compared to spontaneous emission. It is clear that the stimulated emission and absorption rates should be the same from time-reversal symmetry [this can also be seen from Einstein’s famous argument involving an atomic gas in thermal equilibrium with a photon gas, which was used to derive the $A$ and $B$ coefficients; see, for example, Griffiths (1995) or Bransden and Joachain (1989)]. In equilibrium, $dN_g/dt$ and $dN_e/dt$ are zero, and we find that

$$N_e = \frac{\kappa}{1 + 2\kappa}N_{\text{tot}}, \tag{3.162}$$

so the fluorescence intensity is proportional to $\kappa/(1 + 2\kappa)$ (Fig. 3.6).

(b) Now suppose we have a three-level system as shown in Fig. 3.7. The incident light is resonant with the $|g\rangle \rightarrow |e\rangle$ transition and the excited state $|e\rangle$ primarily decays to a metastable level $|m\rangle$ at a rate $\gamma_0$. There is a slow relaxation rate $\gamma_{\text{rel}} \ll \gamma_0$ of the metastable level back to the ground state. The states $|m\rangle$ and $|g\rangle$ could be, for example, different ground state hyperfine levels, and $\gamma_{\text{rel}}$ could be the result of collisional relaxation. Again assume that Doppler broadening may be ignored and that the excitation light is monochromatic.

Calculate the saturation parameter $\kappa$ for this situation, and find the dependence of the fluorescence intensity on $\kappa$.

Solution

The relaxation rate referred to in Eq. (3.156) is generally the slowest relaxation rate in the system, since this process becomes a “bottleneck” for the incoherent
return of atoms to the ground state. Therefore in this case the saturation parameter is given by

\[ \kappa = \frac{d^2 \mathcal{E}^2}{\gamma_0 \gamma_{\text{rel}}}, \]  

(3.163)

since \( \gamma_{\text{rel}} \) is the slowest rate in the problem.

To verify Eq. (3.163) and find the dependence of the spontaneous emission intensity on \( \kappa \) we again write down the appropriate rate equations as we did in

**Fig. 3.6** Fractional population of excited state as a function of the saturation parameter \( \kappa \) for the case described in part (a). The fluorescence intensity \( I_F \) is proportional to \( \gamma_0 N_e \).

**Fig. 3.7** Level diagram for the three-level system considered in part (b).
FIG. 3.8  Fractional population of excited state as a function of the saturation parameter $\kappa$ for the case described in part (b). For the plot we have chosen $\gamma_{rel}/\gamma_0 = 0.2$.

part (a):

$$\frac{dN_g}{dt} = -\Gamma_{pump}N_g + \gamma_{rel}N_m,$$

$$\frac{dN_e}{dt} = +\Gamma_{pump}N_g - \gamma_0N_e,$$

$$\frac{dN_m}{dt} = +\gamma_0N_e - \gamma_{rel}N_m,$$

where we have neglected stimulated emission (since the transition saturates long before stimulated emission becomes important). We also have the condition $N_{tot} = N_g + N_e + N_m$. Setting the time derivatives of the populations equal to zero to obtain the steady state result, after some algebra (and making use of the fact that $\gamma_{rel} \ll \gamma_0$) we find for the excited state population (Fig. 3.8)

$$N_e = \frac{\kappa}{1 + \kappa} \frac{\gamma_{rel}}{\gamma_0} N_{tot}. \quad (3.167)$$

Note that the maximum population in the upper state (obtained for $\kappa \gg 1$) is

$$N_e(\text{max}) = \frac{\gamma_{rel}}{\gamma_0} N_{tot}. \quad (3.168)$$

Again the fluorescence intensity is proportional to $\gamma_0N_e$, so the maximum fluorescence intensity is smaller than in the two-level case by a factor of $2\gamma_{rel}/\gamma_0$, since atoms tend to reside in the “bottleneck” state $|m\rangle$.

(c) Now we discuss the phenomenon of power broadening. Consider the atomic system discussed in part (b) of this problem (Fig. 3.7).
If one scans the frequency of a laser through the atomic resonance at low light powers \[ \kappa \ll 1, \text{ where } \kappa \text{ is given by expression (3.163)} \], one finds that the fluorescence intensity measured as a function of detuning has a Lorentzian lineshape with width \( \gamma_0 \).

What is the dependence of the fluorescence intensity \( I_F(\Delta) \) on detuning for large \( \kappa \)?

**Solution**

As the excitation light is tuned through resonance with the \(|g⟩ \rightarrow |e⟩\) transition, the pumping rate \( \Gamma_{\text{pump}} \) follows a Lorentzian dependence,\(^{10}\) so we have an effective saturation parameter \( \kappa_{\text{eff}}(\Delta) \) that depends on the detuning \( \Delta \) of the light from resonance:

\[
\kappa_{\text{eff}}(\Delta) = \kappa \frac{\gamma^2_0/4}{\Delta^2 + \gamma^2_0/4}, \tag{3.169}
\]

where \( \kappa \) is the resonant saturation parameter [Eq. (3.163)] and the Lorentzian is normalized to unity on resonance. The effective saturation parameter \( \kappa_{\text{eff}}(\Delta) \) can be used directly in the rate equations in place of \( \kappa \), so we obtain from Eq. (3.167) the fluorescence intensity \( I_F(\Delta) \propto \gamma_0 N_e \) as a function of detuning:

\[
I_F(\Delta) \propto \frac{\kappa_{\text{eff}}(\Delta)}{1 + \kappa_{\text{eff}}(\Delta)} \frac{\gamma_{\text{rel}} N_{\text{tot}}}{\gamma^2_0/4} \frac{1}{\Delta^2 + \gamma^2_0/4} \tag{3.170}
\]

\[
I_F(\Delta) = \frac{\gamma^2_0/4}{\Delta^2 + \frac{1}{\gamma^2_0/4} \gamma_{\text{rel}} N_{\text{tot}}} \tag{3.171}
\]

\[
I_F(\Delta) = \frac{\gamma^2_0/4}{\Delta^2 + (1 + \kappa) \gamma^2_0/4 \gamma_{\text{rel}} N_{\text{tot}}} \tag{3.172}
\]

This is just a Lorentzian profile with a width

\[
\gamma = \gamma_0 \sqrt{1 + \kappa} \tag{3.173}
\]

known as the **power-broadened linewidth**.

(d) Finally, we consider how Doppler broadening affects our results. If the atoms in a sample have a thermal distribution of velocities, from the viewpoint of a moving atom the light frequency is shifted by an amount \( \approx \vec{k} \cdot \vec{v} \), where \( \vec{k} \) is the wave vector of the light and \( \vec{v} \) is the atomic velocity. Averaging over all atomic velocities, as

\(^{10}\) This can be seen by calculating the stimulated absorption rate as done in Problem 3.4 without assuming the excitation light is on resonance, but rather using the Lorentzian profile from Eq. (3.79).
When narrow-band excitation light is tuned to frequency $\omega$ within a Doppler-broadened profile, the fluorescence is due to a particular group of atoms with velocities $\vec{v}$ whose Doppler shifts are $\lesssim \gamma$.

mentioned in Problem 3.6, we have for $I_F(\Delta)$ in the limit of large Doppler width $\Gamma_D \gg \gamma_0$:

$$I_F(\Delta) = I_F(0)e^{-\Delta^2/\Gamma_D^2}.$$  \hspace{1cm} (3.174)

In contrast to the previously discussed homogeneous broadening mechanisms such as spontaneous emission and power broadening, Doppler broadening is an example of inhomogeneous broadening – the probability for emission and absorption is not the same for all atoms.

Again consider atoms with the energy level structure shown in Fig. 3.7, but now assume that the atoms have a thermal distribution of velocities. If we tune the narrow-band excitation light to a particular frequency within the Doppler profile, the light primarily interacts with a group of atoms whose velocities are such that the Doppler shifts are less than the homogeneous linewidth. Such a set of atoms is commonly referred to as a velocity group, illustrated in Fig. 3.9.

What is the dependence of fluorescence intensity on $\kappa$ for such a Doppler-broadened medium?

\[\text{\footnotesize\(^{11}\) A more accurate representation of the spectral profile, which takes into account both homogeneous and inhomogeneous broadening mechanisms is the Voigt profile, which is a convolution of Lorentzian and Gaussian profiles [see, for example, Demtröder (1996) and Khriplovich (1991)].}\]
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Solution

The fraction $\delta N$ of the total number of atoms $N_{\text{tot}}$ with which the light interacts is

$$\delta N \sim \frac{\gamma}{\Gamma_D} N_{\text{tot}}, \quad (3.175)$$

where $\gamma$ is the homogeneous linewidth. For the considered case, $\gamma$ is the power-broadened linewidth given by Eq. (3.173). Otherwise, the rate equations for the resonant velocity group remain the same as those considered in part (b), and we have:

$$I_F \propto \frac{\kappa}{1 + \kappa} \delta N \propto \frac{\kappa}{\sqrt{1 + \kappa}} \frac{\gamma_0}{\Gamma_D} N_{\text{tot}}. \quad (3.176)$$

Note that in contrast to the Doppler-free case, the fluorescence intensity continues to increase ($\propto \sqrt{\kappa}$) even for $\kappa \gg 1$. This continues as long as $\gamma_0 \sqrt{1 + \kappa} \ll \Gamma_D$. In the opposite limit, $\gamma_0 \sqrt{1 + \kappa} \gg \Gamma_D$, Doppler broadening may be ignored.

3.8 Angular distribution and polarization of atomic fluorescence

Atoms are prepared in the $M_{J'} = 1/2$ Zeeman sublevel of an excited state with angular momentum $J' = 1/2$, from which they spontaneously decay to a lower state that also has $J = 1/2$. No external fields are applied.

(a) What is the angular distribution of the emitted light intensity?

(b) What is the polarization state of the light emitted in a given direction?

Hint

See Appendix D explaining how to specify light polarization states.

Solution

(a) Assume that the atoms are at the origin of a Cartesian frame. The problem has axial symmetry with respect to the quantization axis $(\hat{z})$, so it is sufficient to only consider radiation emitted in the direction whose vector lies in the $x > 0, \ xz$-semiplane. The direction of light propagation is therefore completely defined by the polar angle $\theta$ (Fig. 3.10). For a given $\theta$, two independent, orthogonal light
polarization directions can be chosen: \( \hat{\epsilon}_1 = \hat{y} \) and
\[
\hat{\epsilon}_2 = \hat{\theta} \equiv \cos \theta \hat{x} - \sin \theta \hat{z},
\]
which are directions orthogonal to the light propagation along \( \hat{k} \) (Fig. 3.10).

There are two possible decay channels (Fig. 3.11). The amplitude \( A \) of the emission with a given polarization \( \hat{\epsilon} \) into the final state \( |J = 1/2, M_J = 1/2\rangle \) is
\[
A \propto \langle J = 1/2, M_J | \hat{\epsilon} \cdot \vec{r} | J' = 1/2, M'_J = 1/2 \rangle.
\]
(3.178)

According to the Wigner-Eckart theorem (Appendix F), only the \( q = 0 \) spherical component of \( \hat{\epsilon} \) contributes to \( A \) for the decay to \( M_J = 1/2 \), and only the \( q = +1 \) component of \( \hat{\epsilon} \) (which picks out the \( q = -1 \) component of \( \vec{r} \), see Eq. (F.30) in Appendix F) contributes to \( A \) for the decay to \( M_J = -1/2 \). The amplitude \( A \) is proportional to the corresponding Clebsch-Gordan coefficients, which are
\[
\langle 1/2, 1/2, 1, -1|1/2, -1/2 \rangle = \sqrt{2} \sqrt{3}/3
\]
(3.179)
for the \( \sigma_+ \) emission and
\[
\langle 1/2, 1/2, 1, 0|1/2, 1/2 \rangle = \sqrt{1} \sqrt{3}/3
\]
(3.180)
for \( \pi \) emission.

Let us first consider the \( \pi \) emission. In a classical picture, such emission is produced by a dipole oscillating along \( z \) (at the transition frequency). We can therefore expect that the largest emission intensity is in the equatorial plane (\( \theta = \pi/2 \)), and that there is no emission along \( z \) (\( \theta = 0, \pi \)). These expectations are confirmed by the exact expressions. The intensity of the emission with a given

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**Fig. 3.10** Coordinate system for analysis of atomic fluorescence: \( \hat{k} \) is the light propagation direction, \( \hat{y} \) (pointing into the page) and \( \hat{\theta} \) are orthogonal light polarization directions. Because of cylindrical symmetry, we need only consider the \( xz \)-plane.
Atoms in the excited state $J = 1/2, M_J = 1/2$ can decay to either one of the two Zeeman sublevels of the lower $J = 1/2$ state (the $\pi$ and $\sigma^+$ emissions, respectively). The numbers indicate relative overall intensity of the emissions proportional to the squares of the corresponding Clebsch-Gordan coefficients.

polarization vector for a given $\theta$ (as we have introduced above) is proportional to the square of the scalar product of the corresponding polarization vector and $\hat{z}$:

$$I^{(\pi)}_y(\theta) \propto |\hat{y} \cdot \hat{z}|^2 = 0 ; \quad (3.181)$$

$$I^{(\pi)}_\theta(\theta) \propto |\hat{\theta} \cdot \hat{z}|^2 = |(\cos \theta \hat{x} - \sin \theta \hat{z}) \cdot \hat{z}|^2 = \sin^2 \theta . \quad (3.182)$$

Thus the overall intensity is $I^{(\pi)}_{\text{tot}}(\theta) \propto \sin^2 \theta$.

Now consider the $\sigma^+$ emission. In a classical picture, such emission is produced by a dipole rotating (rather than oscillating) in the $xy$-plane. We can therefore expect that the largest emission intensity is along $z$ ($\theta = 0, \pi$), while in the equatorial plane ($\theta = \pi/2$), the emission should have one half of the intensity. (This is because the dipole’s rotation can be decomposed into two orthogonal oscillations, and only one of them is “seen” from the equatorial plane.) These expectations are again confirmed by the calculation. Using the polarization vector for the $\sigma^+$ emission in the form

$$\hat{\epsilon}^+ = \frac{1}{\sqrt{2}} (\hat{x} + i \hat{y}) , \quad (3.183)$$

we have

$$I^{(\sigma)}_y(\theta) \propto |\hat{y} \cdot \hat{\epsilon}^+|^2 = \left| \hat{y} \cdot \frac{1}{\sqrt{2}} (\hat{x} + i \hat{y}) \right|^2 = \frac{1}{2} ; \quad (3.184)$$

$$I^{(\sigma)}_\theta(\theta) \propto |\hat{\theta} \cdot \hat{\epsilon}^+|^2 = \left| (\cos \theta \hat{x} - \sin \theta \hat{z}) \cdot \frac{1}{\sqrt{2}} (\hat{x} + i \hat{y}) \right|^2 = \frac{\cos^2 \theta}{2} \quad (3.185)$$
Fig. 3.12 Normalized angular distributions of fluorescence intensity for \( \pi \) emission (dot-dashed line), \( \sigma \) emission (dashed line), and the overall distribution (solid line), which is isotropic in the present case.

The total intensity of the \( \sigma \)-emission is

\[
I_{\text{tot}}^{(\sigma)}(\theta) \propto I_y^{(\sigma)}(\theta) + I_\theta^{(\sigma)}(\theta) = \frac{1 + \cos^2 \theta}{2}.
\] (3.186)

To find the overall intensity of radiation in a given direction, we need to add the two contributions, \( I_{\text{tot}}^{(\pi)}(\theta) \) and \( I_{\text{tot}}^{(\sigma)}(\theta) \), weighted by the total probability of the corresponding emissions (1/3 and 2/3, respectively). The result is independent of \( \theta \), meaning that the total light intensity is emitted isotropically.

The normalized angular distributions for the \( \pi \) and \( \sigma \) light and the overall isotropic distributions are shown in Fig. 3.12.

(b) Even before any calculations, it is clear that for \( \theta = 0 \) or \( \pi \), only the \( \sigma \) light is seen, and therefore light is completely circularly polarized. In the equatorial plane (\( \theta = \pi/2 \)), equal amounts of independent contributions of the vertically polarized \( \pi \) light and horizontally polarized \( \sigma \) light are seen, so the light is unpolarized.

For a general value of \( \theta \), a horizontally oriented polarizer (along \( \hat{y} \)) will transmit an intensity \( \propto 1/2 \) from the \( \sigma \) light, while a vertically oriented polarizer (along \( \hat{\theta} \)) will transmit an intensity \( \propto (\cos^2 \theta)/2 \) from the \( \sigma \) light and \( \propto (\sin^2 \theta)/2 \) from the
π light. Thus for the first Stokes parameter (Appendix D) we have:

\[ S_1 = \frac{I_x - I_y}{I_0} = \frac{1 - \cos^2 \theta - \sin^2 \theta}{2} = 0. \]  

(3.187)

From symmetry, it is clear that \( S_2 = 0 \) also. The linearly polarized π light cannot contribute to \( S_3 \). From the discussion in part (a) [in particular Eqs. (3.184) and (3.185)], we also see that the vector amplitude of the \( \sigma^+ \) light emitted in a given direction can be written in the form

\[ -i \frac{\sqrt{2}}{\sqrt{2}} \hat{y} = \cos \theta \hat{\theta} \propto \frac{1}{\sqrt{2}} \left( \hat{y} - i \cos \theta \hat{\theta} \right), \]  

(3.188)

where we have removed the overall phase factor. By taking the scalar product of this amplitude with the amplitude vectors

\[ \epsilon'_+ = -\frac{1}{\sqrt{2}} \left( \hat{y} + i\hat{\theta} \right) \]  

(3.189)

for the left-circular polarization\(^{12}\) and

\[ \epsilon'_- = \frac{1}{\sqrt{2}} \left( \hat{y} - i\hat{\theta} \right) \]  

(3.190)

for the right-circular polarization, we find that

\[ S_3 = \frac{I_+ - I_-}{I_0} = \frac{(1 + \cos \theta)^2 - (1 - \cos \theta)^2}{4} = \cos \theta. \]  

(3.191)

This shows that light emitted with \( \theta = 0 \) is left-circularly polarized, while light emitted with \( \theta = \pi \) is right-circularly polarized. The degree of polarization is

\[ p = |\cos \theta| \]  

in agreement with our qualitative argument above.

### 3.9 Change in absorption due to optical pumping

For \( J = 1 \rightarrow J' \) electric dipole \((E1)\) transitions (with \( J' = 0, 1, 2 \)), find the relative changes in populations of the \( J = 1 \) Zeeman sublevels as a result of optical pumping with linearly polarized light (assume the quantization axis along the axis of light polarization, i.e., π-polarization). Assume “closed” transitions (i.e., atoms excited to the upper level can only decay back to the lower level), that the excitation light is on resonance, the medium is optically thin, and that, in order to simplify

\(^{12}\) The circular polarization vectors \( \epsilon'_+ \) and \( \epsilon'_- \) are defined to be orthogonal to \( \hat{k} \), and we identify \( \hat{y} \) as the horizontal direction and \( -\hat{\theta} \) as the vertical direction to form an appropriate right-handed coordinate system [compare with Eq. (3.183)].
calculations, the optical pumping saturation parameter $\kappa$ (see Problem 3.7) is much less than one [assume a relaxation rate $\gamma_{\text{rel}} \ll \gamma_0$ between the ground state Zeeman sublevels, where $\gamma_0$ is the spontaneous decay rate (Problem 3.3)].

Verify that for the $J = 1 \rightarrow J' = 0, 1$ cases, optical pumping leads to reduction of further light absorption by the medium, while in the $J = 1 \rightarrow J' = 2$ case the opposite is true: absorption increases as a result of optical pumping. This is a general property of $J \rightarrow J + 1$ transitions (as opposed to $J \rightarrow J - 1, J$ transitions) that holds for arbitrary light polarization [Kazantsev et al. (1985)]. Note that although we assume $\kappa$ small in this problem, the qualitative conclusion, that optical pumping reduces absorption for $J \rightarrow J - 1, J$ transitions and increases absorption for closed $J \rightarrow J + 1$ transitions, holds for any $\kappa$.

**Solution**

As is often the case, it is helpful to think about a related problem that permits a simple solution in order to understand the basic effect. Consider optical pumping with circularly polarized light in the limit of large $\kappa$. (As noted in the statement of the problem, it turns out that the general result is independent of light polarization and holds for any $\kappa$.) As Fig. 3.13 shows, for the $1 \rightarrow 0, 1$ transitions, the atoms will end up in states that do not absorb light (so-called dark states). However, for the $1 \rightarrow 2$ transition, the atoms are pumped into a state that absorbs light (a bright state).

According to the results of Problem 3.4, the absorption rate is proportional to the square of the Clebsch-Gordan coefficient describing the coupling between lower state and upper state. For a $J = 1 \rightarrow J' = 2$ transition and $\sigma_+$ polarization, the relevant Clebsch-Gordan coefficients are:

$$
\langle J, M, 1, 1 | J', M' = M + 1 \rangle^2 = \frac{1}{6} \left( |1, -1 \rangle \rightarrow |2, 0 \rangle \right), \quad (3.192)
$$

$$
= \frac{1}{2} \left( |1, 0 \rangle \rightarrow |2, 1 \rangle \right), \quad (3.193)
$$

$$
= 1 \left( |1, 1 \rangle \rightarrow |2, 2 \rangle \right). \quad (3.194)
$$

Thus the atoms are pumped into a state that has a stronger coupling to the light field, leading to increased absorption!

Prior to considering the specific cases, we outline the general approach to the problem. The first task is to determine the manner in which the light redistributes the population among the various ground state Zeeman sublevels, which is rather tricky for the general case. To find the density of atoms $\rho_0(M)$ in a particular ground state sublevel $|J, M\rangle$, we must find the rate at which atoms are being excited from $|J, M\rangle$ and the flux $F_{\text{sp}}(M)$ of atoms decaying back to $|J, M\rangle$ via spontaneous emission from all the various excited state Zeeman sublevels $|J', M'\rangle$.
Fig. 3.13 Illustration of the effects of optical pumping with $\sigma_+$ (left-circularly polarized) light on the populations of ground state Zeeman sublevels for closed $J = 1 \rightarrow J' = 0, 1, 2$ transitions.

(whose populations $\rho_g(M')$ depend on populations and rates of excitation from the other ground state sublevels).

The basic rate equation for a given ground-state Zeeman sublevel is

$$\frac{d\rho_g(M)}{dt} = -W_{eg}(M)\rho_g(M) + F_{sp}(M) + \gamma_{rel}[\rho_g(\text{avg}) - \rho_g(M)], \quad (3.195)$$

where $W_{eg}(M)$ is the excitation rate from a given ground state sublevel $|J, M\rangle$ for $\pi$-polarized light and $\rho_g(\text{avg})$ is the average population of a Zeeman sublevel. In
The condition \( \kappa \ll 1 \) allows us to say that the excitation rate is significantly smaller than the ground state relaxation rate \( \gamma_{\text{rel}} \), so

\[
\rho_g(M) \approx \rho_g(\text{avg}) + \frac{F_{\text{sp}}(M)}{\gamma_{\text{rel}}} - \frac{W_{eg}(M)}{\gamma_{\text{rel}}}.
\] (3.197)

From the results of Problem 3.4 [Eq. (3.132)], we see that the excitation rate \( W_{eg}(M) \) for \( \pi \)-polarized light is

\[
W_{eg}(M) = \frac{|\langle e, J | d || g, J \rangle|^2 \varepsilon_0^2}{2J' + 1} \gamma_0 \langle J, M, 1, 0 | J', M' \rangle^2
\] (3.198)

where we have made use of the fact that for \( \pi \)-polarized light the Clebsch-Gordan coefficients vanish unless \( M = M' \) and we have set \( \hbar = 1 \).

The flux of atoms \( F_{\text{sp}}(M) \) spontaneously decaying back to \( |J, M\rangle \) is given by

\[
F_{\text{sp}}(M) = \frac{\gamma_0}{2J + 1} \sum_{M'} \sum_{q} \rho_e(M') \langle J', M', 1, q | J, M \rangle^2,
\] (3.199)

where \( q = 1, 0, -1 \) to allow for all possible polarizations of spontaneously emitted photons. For \( \kappa \ll 1 \), we can follow the same basic approach as applied in part (b) of Problem 3.7 to see that the excited state population \( \rho_e(M') \) is given approximately by

\[
\rho_e(M') \approx \rho_g(M') \frac{|\langle e, J' | d || g, J \rangle|^2 \varepsilon_0^2}{2J' + 1} \gamma_0 \langle J, M', 1, 0 | J', M' \rangle^2
\] (3.200)

\[
\approx \rho_g(\text{avg}) \frac{|\langle e, J' | d || g, J \rangle|^2 \varepsilon_0^2}{2J' + 1} \gamma_0 \langle J, M', 1, 0 | J', M' \rangle^2,
\] (3.201)

where we have assumed that since \( \kappa \) is small, the ground state populations do not change significantly. Therefore

\[
F_{\text{sp}}(M) \approx \rho_g(\text{avg}) \frac{|\langle e, J' | d || g, J \rangle|^2 \varepsilon_0^2}{\gamma_0 (2J + 1)}
\]

\[
\times \sum_{M'} \sum_{q} \langle J, M', 1, 0 | J', M' \rangle^2 \langle J', M', 1, q | J, M \rangle^2.
\] (3.202)

From Eqs. (3.197), (3.198), and (3.202), we see that the fractional change in the populations of the ground state Zeeman sublevels

\[
\delta \rho_g(M) = \frac{\rho_g(M) - \rho_g(\text{avg})}{\rho_g(\text{avg})}
\] (3.203)
is described by
\[
\delta \rho_g(M) \approx \kappa \left[ \left( \sum_{M'} \sum_q \frac{\langle J, M', 1, 0|J', M'\rangle^2 \langle J', M', 1, q|J, M\rangle^2}{2J + 1} \right) - \frac{\langle J, M, 1, 0|J', M\rangle^2}{2J' + 1} \right],
\]
where the saturation parameter \( \kappa \) is defined here to be
\[
\kappa \equiv \frac{|\langle e, J'|d||g, J \rangle|^2 E_0^2}{\gamma_0 \gamma_{rel}}.
\]

Now we are ready to consider the specific cases.

**The 1 \rightarrow 0 case:** Since there is only one excited state Zeeman sublevel, only one of the ground state Zeeman sublevels, namely \( M = 0 \), interacts with the pump light (see Fig. 3.14). Atoms excited to the upper state decay with equal likelihood to any of the ground state sublevels. This can be deduced from the isotropy of space, since atoms in the \( |0, 0\rangle \) state are unpolarized, and spontaneous emission cannot create polarization where none previously existed [otherwise the vacuum, which induces spontaneous emission (Problems 3.2 and 3.3), would have a preferential direction!]. Therefore, the optical pumping process must decrease the population \( \rho_g(0) \) and increase \( \rho_g(\pm 1) \).

This reasoning is quickly confirmed using formula (3.204):
\[
\delta \rho_g(0) \approx -\frac{2\kappa}{9},
\]
\[
\delta \rho_g(\pm 1) \approx +\frac{\kappa}{9}.
\]

It is clear that optical pumping decreases absorption of the excitation light in the 1 \rightarrow 0 case, since the population of the only ground state Zeeman sublevel that interacts with the light (the *bright state*) decreases, while the populations of states which do not interact with the light (the *dark states*) increase.

**The 1 \rightarrow 1 case:** In this case two ground state sublevels (\( M = 1 \) and \( M = -1 \)) interact with the pump light while the \( M = 0 \) sublevel is a dark state (Fig. 3.14). The \( |J = 1, M = 0\rangle \rightarrow |J' = 1, M' = 0\rangle \) transition is forbidden because the Clebsch-Gordan coefficient \( (1, 0, 1, 0|1, 0) \) vanishes (this is derived and explained in Problem 9.5). The transition rates from the \( M = 1 \) and \( M = -1 \) ground state sublevels are the same, and there is some probability for atoms excited to the upper states to decay to the dark state \( |J = 1, M = 0\rangle \). Thus optical pumping decreases absorption in this situation as well.
CHANGE IN ABSORPTION DUE TO OPTICAL PUMPING

\[ M = -2 \quad M = 1 \quad M = 0 \quad M = 1 \quad M = 2 \]

**Fig. 3.14** Illustration of the effects of optical pumping with linearly polarized (π) light on the populations of ground state Zeeman sublevels for closed \( J \rightarrow J' = 0, 1, 2 \) transitions.

Again, Eq. (3.204) supports our intuitive argument:

\[
\delta \rho_g(0) \approx \frac{\kappa}{6}, \quad (3.208)
\]

\[
\delta \rho_g(\pm 1) \approx -\frac{\kappa}{12}. \quad (3.209)
\]

**The 1 \rightarrow 2 case**: In this case, all three ground state Zeeman sublevels interact with the pump light, i.e., there are no dark states. The strength of the interaction with the pump light varies between the states, as can be seen by comparing the
appropriate Clebsch-Gordan coefficients. This situation is sufficiently complicated that our formula (3.204) will pay dividends, as we can use it to readily compute the relative change in the ground state populations:

\[ \delta \rho_g(0) \approx + \frac{\kappa}{18}, \quad (3.210) \]

\[ \delta \rho_g(\pm 1) \approx - \frac{\kappa}{36}. \quad (3.211) \]

We see that the population of the \( M = 0 \) ground state Zeeman sublevel increases, while the populations of the other sublevels decrease.

From Eq. (3.198), we see that the larger the square of the Clebsch-Gordan coefficient \( \langle J, M, 1, 0 | J', M \rangle^2 \), the higher the rate of absorption. If one computes the Clebsch-Gordan coefficients for the \( 1 \to 2 \) transition, it is found that the \( M = 0 \) sublevel has the largest absorption rate -- therefore, in contrast to the \( 1 \to 0 \) and \( 1 \to 1 \) transitions, optical pumping increases light absorption in this case, just as for the case of circularly polarized light.

Note that, because of the effects discussed in this problem, closed \( J \to J + 1 \) transitions only “bleach” when the flux of photons absorbed equals the flux of photons generated by stimulated emission, i.e., when

\[ \frac{d^2 E_0^2}{\gamma_0^2} \sim 1. \quad (3.212) \]

This is in contrast to \( J \to J - 1 \), \( J \) transitions which bleach when all the atoms are pumped into dark states, i.e., when

\[ \frac{d^2 E_0^2}{\gamma_0 \gamma_{\text{rel}}} \sim 1. \quad (3.213) \]

### 3.10 Optical pumping and the density matrix

Atoms which are initially in an unpolarized ground state with \( J = 3/2 \) are subject to optical pumping with light which is near-resonant with a transition to an excited state with \( J' = 1/2 \). Assuming that all atoms excited to the \( J' = 1/2 \) state decay to a “trap” state other than the ground state and that other relaxation processes can be neglected, find the \( 4 \times 4 \) density matrix describing the Zeeman sublevels of the \( J = 3/2 \) state after the optical pumping is complete (see Appendix G for more details about the density matrix, as well as a discussion of the polarization moments created by optical pumping in the case considered here). Consider the following two cases of light polarization:

(a) left circular polarization (\( \sigma_+ \)),

(b) right circular polarization (\( \sigma_- \)).
OPTICAL PUMPING AND THE DENSITY MATRIX

(b) linear polarization along $z$,  
(c) linear polarization along $x$.

Solution

(a) In this case, the states with $M_J = -3/2$ and $M_J = -1/2$ will be completely pumped out and the remaining two sublevels will not be affected by optical pumping in any way (Fig. 3.15). Choosing the normalization in such a way that the initial population for each Zeeman sublevel is equal to one, we can write for the final ground state density matrix:

$$
\rho = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix},
$$

(3.214)

where the matrix indices correspond to the $M_J$ components in decreasing order.

(b) In this case, the light couples states with $M_J = M'_J$, so the $M_J = \pm 1/2$ states are depleted (Fig. 3.16). Thus we have for the resultant ground state density matrix:

$$
\rho = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}.
$$

(3.215)

(c) Here, it is sufficient to notice that all atoms get pumped out of the ground state except the ones that are in the two possible $x$-nonabsorbing (dark) states $|\psi_+^{\pm}\rangle$ that are formed by coherent superpositions of the sublevels pairs $M_J = -3/2$ and $M_J' = -1/2$.

![Figure 3.15](image-url)

**Fig. 3.15** Optical pumping of a $J = 3/2 \rightarrow J' = 1/2$ transition with left-circularly polarized light.
F. 3.16 Optical pumping of a $J = 3/2 \rightarrow J' = 1/2$ transition with linearly polarized light.

F. 3.17 Optical pumping of a $J = 3/2 \rightarrow J' = 1/2$ transition with $x$-polarized light.

$-3/2, M_J = 1/2$ and $M_J = -1/2, M_J = 3/2$ (Fig. 3.17). This effect, where population remains in a superposition of Zeeman sublevels even though all the Zeeman sublevels are coupled to the light field, is known as coherent population trapping. As we shall see, despite the fancy name, the only difference between this case and the one considered in part (b) of the problem is the choice of quantization axis.

An atom is in a dark state $|\psi_d\rangle$ when the $E1$-amplitudes of excitation to the upper state sublevels are zero, i.e.,

$$\langle J' = 1/2, M'_J = \pm 1/2 | e\mathcal{E}(t)\mathbf{\hat{r}} \cdot \mathbf{\hat{\varepsilon}} | \psi_d\rangle = 0 . \quad (3.216)$$

Here $H = -\mathbf{\hat{d}} \cdot \mathcal{E}(t) = e\mathcal{E}(t)\mathbf{\hat{r}} \cdot \mathbf{\hat{\varepsilon}}$ is the Hamiltonian describing the atom-light interaction, $\mathbf{\hat{\varepsilon}}$ is the light polarization vector, and for $M'_J = 1/2$,

$$|\psi^+_d\rangle = C_{-1/2} |J = 3/2, M_J = -1/2 \rangle + C_{3/2} |J = 3/2, M_J = 3/2 \rangle , \quad (3.217)$$

and for $M'_J = -1/2$

$$|\psi^-_d\rangle = C_{-3/2} |J = 3/2, M_J = -3/2 \rangle + C_{1/2} |J = 3/2, M_J = 1/2 \rangle . \quad (3.218)$$

The interaction Hamiltonian can be written in terms of spherical tensors in order to take advantage of the Wigner-Eckart theorem (Appendix F). In this case
OPTICAL PUMPING AND THE DENSITY MATRIX

$\hat{\varepsilon} = \hat{x}$, so we can use Eqs. (F.23) and (F.25) to write

$$x = \frac{1}{\sqrt{2}} (r_- - r_+) , \quad (3.219)$$

thus

$$H = \frac{e\hat{E}(t)}{\sqrt{2}} (r_- - r_+) \quad (3.220)$$

where $r_\pm$ are the $q = \pm 1$ components of the vector operator $\vec{r}$ in the spherical basis.

Returning to Eq. (3.216) and using the Wigner-Eckart theorem (F.1)

$$\langle J', M'_J | r_\pm | J, M_J \rangle = \langle J', | r \rangle | J \rangle \sqrt{2J' + 1} \langle J, M_J, \pm 1 | J', M'_J \rangle \quad (3.221)$$

along with Eqs. (3.217) and (3.218), we obtain the conditions

$$\langle 3/2, 3/2, 1, -1|1/2, 1/2 \rangle C_{3/2} - \langle 3/2, -1/2, 1, 1|1/2, 1/2 \rangle C_{-1/2} = 0 , \quad (3.222)$$

$$\langle 3/2, 1/2, 1, -1|1/2, -1/2 \rangle C_{1/2} - \langle 3/2, -3/2, 1, 1|1/2, -1/2 \rangle C_{-3/2} = 0 . \quad (3.223)$$

These Clebsch-Gordan coefficients have the following values:

$$\langle 3/2, 3/2, 1, -1|1/2, 1/2 \rangle = \frac{1}{\sqrt{2}} , \quad (3.224)$$

$$\langle 3/2, -1/2, 1, 1|1/2, 1/2 \rangle = \frac{1}{\sqrt{6}} , \quad (3.225)$$

$$\langle 3/2, 1/2, 1, -1|1/2, -1/2 \rangle = \frac{1}{\sqrt{6}} , \quad (3.226)$$

$$\langle 3/2, -3/2, 1, 1|1/2, -1/2 \rangle = \frac{1}{\sqrt{2}} , \quad (3.227)$$

from which we obtain

$$C_{-1/2} = C_{3/2} \sqrt{3} , \quad (3.228)$$

$$C_{1/2} = C_{-3/2} \sqrt{3} . \quad (3.229)$$

We can also construct two linear combinations of the Zeeman sublevels which are orthogonal to the dark states $|\psi_d^\pm \rangle$; these will be bright states, which – by analogy with part (b) – will be completely depleted by the optical pumping. We
can find the correct normalization for the density matrix by using the fact that the dark states each have unit population before and after optical pumping. Thus, we find

\[
\rho = \frac{1}{4} \begin{pmatrix}
1 & 0 & \sqrt{3} & 0 \\
0 & 3 & 0 & \sqrt{3} \\
\sqrt{3} & 0 & 3 & 0 \\
0 & \sqrt{3} & 0 & 1
\end{pmatrix}.
\]

(3.230)

We note that this solution can also be obtained by rotating the density matrix obtained in part (b) by \(\pi/2\) about the \(y\)-axis (using the appropriate quantum mechanical rotation matrix – see Appendix E). Indeed, the dark states \(|\psi^+_d\rangle\) are simply found by applying such a rotation to the states \(|J = 3/2, M_J = \pm 3/2\rangle\).

### 3.11 Cascade decay

Consider an atom which has an excited state \(|a\rangle\) of the same parity as the ground state \(|g\rangle\) (Fig. 3.18) which decays to an opposite-parity state \(|b\rangle\) which in turn decays to the ground state. Suppose initially states \(|a\rangle\) and \(|b\rangle\) are not populated. Then at time \(t = t_0\), \(|a\rangle\) is instantly populated. Suppose also that in an experiment, one detects fluorescence on the \(|b\rangle \rightarrow |g\rangle\) transition and the detection system is insensitive to fluorescence at the wavelength of the \(|a\rangle \rightarrow |b\rangle\) transition.

(a) Derive the time dependence of the fluorescence signal in terms of the lifetimes of states \(|a\rangle\) and \(|b\rangle\) (\(\tau_a\) and \(\tau_b\), respectively).

(b) Analyze the limiting cases: \(\tau_a \gg \tau_b\), \(\tau_a \ll \tau_b\), and \(\tau_a \approx \tau_b\).
Fig. 3.19  Fluorescence on the Dy $|b\rangle \rightarrow |g\rangle$ transition as a function of time (the fluorescence peak appears upside down in the figure because the output of the photomultiplier has negative polarity).

(c) Will the above analysis change if $|a\rangle$ has additional decay channels to states other than $|b\rangle$?

(d) Figure 3.19 shows actual data from an experiment with atomic dysprosium (Budker et al. 1994). The state $|a\rangle$ ($E = 19797.96$ cm$^{-1}$) was populated with a sequence of two short (duration $\sim$7 ns) laser pulses. Fluorescence on the $|b\rangle \rightarrow |g\rangle$ transition was detected with a fast photomultiplier. An interference filter was used to select fluorescence on the $|b\rangle \rightarrow |g\rangle$ transition at 564 nm. The data points on the figure were fit to the expected time dependence (derived in part (a) of this problem); the free parameters of the fit were: $t_0$, the overall signal amplitude, $\tau_a$, and $\tau_b$. Using the figure, estimate $\tau_a$ and $\tau_b$.

Solution

(a) Let us designate the populations of the states $|a\rangle$ and $|b\rangle$ as $\rho_a$ and $\rho_b$, correspondingly. The population of $|a\rangle$ exponentially decays due to spontaneous emission to $|b\rangle$, therefore:

$$\rho_a(t) = \rho_a(t_0) e^{-(t-t_0)/\tau_a}.$$  \hspace{1cm} (3.231)

The differential equation describing the time dependence of $\rho_b(t)$ has a term describing population of $|b\rangle$ via spontaneous emission from $|a\rangle$ and depopulation
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of \(|b\rangle\) by decay to the ground state:

$$\dot{\rho}_b(t) = -\frac{\rho_b}{\tau_b} = \rho_a(t_0) \frac{e^{-(t-t_0)/\tau_a}}{\tau_a} - \frac{\rho_b}{\tau_b}. \quad (3.232)$$

Equation (3.232) is an inhomogeneous linear differential equation. Its solution is the sum of the general solution of the homogeneous equation

$$\dot{\rho}_b(t) = -\frac{\rho_b}{\tau_b} \quad (3.233)$$

and a particular solution of Eq. (3.232). The latter can be found by forcing upon \(\rho_b(t)\) a time dependence of the form \(e^{-(t-t_0)/\tau_a}\). The constant factors in the solution of Eq. (3.232) are determined by the initial conditions: \(\rho_b(t_0) = 0\) and \(\rho_b(t_0) = \rho_a(t_0)/\tau_a\). One therefore arrives at the following expression for \(\rho_b(t)\):

$$\rho_b(t) = \frac{\tau_a}{\tau_a - \tau_b} \rho_a(t_0) \left( e^{-(t-t_0)/\tau_a} - e^{-(t-t_0)/\tau_b} \right). \quad (3.234)$$

The fluorescence signal \(F\) observed in the experiment is proportional to the rate at which atoms return to the ground state from \(|b\rangle\) (this is the number of photons per second emitted on the \(|b\rangle \rightarrow |g\rangle\) transition):

$$F \propto \rho_b(t) \tau_b = \frac{\rho_a(t_0)}{\tau_a - \tau_b} \left( e^{-(t-t_0)/\tau_a} - e^{-(t-t_0)/\tau_b} \right). \quad (3.235)$$

(b) If \(\tau_a \ll \tau_b\), the atoms quickly (i.e., during time \(\sim \tau_a\)) decay into state \(|b\rangle\) and the trailing edge of the fluorescence pulse will be an exponential determined by \(\tau_b\). If \(\tau_a \gg \tau_b\), the “bottleneck” is the decay of \(|a\rangle\) and at \(t \gg \tau_b\) fluorescence decays with time constant \(\tau_a\).

To analyze the case \(\tau_a \approx \tau_b \approx \tau\), set \(\tau_a = \tau_b + \delta \tau\). Then from Eq. (3.234) we have:

$$\rho_b(t) \approx \frac{\tau}{\delta \tau} \rho_a(t_0) e^{-(t-t_0)/\tau} \left( 1 - e^{-\delta \tau (t-t_0)/\tau^2} \right)$$

$$\approx \frac{\tau}{\delta \tau} \rho_a(t_0) e^{-(t-t_0)/\tau} \frac{\delta \tau (t - t_0)}{\tau^2}$$

$$\approx \frac{(t - t_0)}{\tau} \rho_a(t_0) e^{-(t-t_0)/\tau}, \quad (3.236)$$

where we used the Taylor expansion of the exponential valid for

$$\delta \tau (t - t_0)/\tau^2 \ll 1.$$

For greater \(t\)'s, the fluorescence signal just decays exponentially. Therefore, even though Eq. (3.235) may look somewhat singular at \(\tau_a = \tau_b\), nothing special happens in this limit.
COHERENT LASER EXCITATION

3.12 Coherent laser excitation

Consider a $J = 0 \rightarrow J' = 1$ atomic transition which is closed in the sense that all atoms excited to the upper $J' = 1$ state decay back to the lower $J = 0$ state. Suppose that the atoms are illuminated with cw, narrow-band, resonant light which is $\sigma_+$-circularly polarized and that the saturation parameter (Problem 3.7) is very large: $\kappa \gg 1$, for example, $\kappa = 1000$.

(a) What are the time-averaged probabilities of finding atoms in each of the four Zeeman sublevels: $|1, 0\rangle$, $|1, \pm 1\rangle$ and $|0, 0\rangle$?

(b) Same as in part (a), but now suppose that the light, rather than being purely circularly polarized, has a small coherent admixture of the opposite ($\sigma_-$) circular polarization. The intensity of the $\sigma_-$ admixture is 1% of the intensity of the $\sigma_+$ light.

(c) Same, but now assume that the $\sigma_+$ light is blocked out with a circular polarizer, so the atoms only see the $\sigma_-$ light of the same intensity as in part (b).

Solution

(a) No atoms are excited to either of the $|1, -1\rangle$, $|1, 0\rangle$ sublevels, so their population is zero. On the other hand, the transition between the $|0, 0\rangle$ and $|1, 1\rangle$ sublevels is fully saturated (Problem 3.7), so the time-averaged population is approximately 1/2 in each of the sublevels, assuming that the total population is one.

(b) The light now excites a coherent superposition of the $|1, \pm 1\rangle$ upper state sublevels of the form

$$
\psi_e \approx |1, 1\rangle + a|1, -1\rangle,
$$

(3.237)

where $|a|^2 = 0.01$, and the phase of $a$ is determined by the relative phase of the two coherent circular components of the light.

Because the overall light intensity is as large as in part (a), the transition is still saturated, so the upper state (3.237) has time-averaged population $\approx 1/2$ and the populations of the $|1, 1\rangle$ and $|1, -1\rangle$ sublevels are $\approx 1/2$ and $\approx 0.01 \times 1/2$, respectively.
(c) The light now excites only the \( |1, -1\rangle \) upper state sublevel. Since 1% of the \( \sigma_+ \) intensity still corresponds to a large saturation parameter \( \kappa = 0.01 \times 1000 = 10 \), the time-averaged population of the \( |1, -1\rangle \) sublevel is \( \approx 1/2 \).

A similar increase in the population of this sublevel compared to part (b) can be achieved if instead of blocking the \( \sigma_+ \) component a magnetic field is applied that splits the \( J' = 1 \) sublevels and the light frequency is tuned to be in resonance only with the \( |1, 0\rangle \rightarrow |1, -1\rangle \) transition.

The comparison of the cases (b) and (c) shows that the rate of a light-induced transition (in this case, \( |0, 0\rangle \rightarrow |1, -1\rangle \)) strongly depends on the presence of a resonant light field applied to an adjacent transition (in this case, \( |0, 0\rangle \rightarrow |1, 1\rangle \)). This effect belongs to a broad class of phenomena which includes electromagnetically induced transparency (Kocharovskaya 1992, Harris 1997) and are based on coherent interactions of multicomponent light with multiple states of a quantum system (atoms, molecules, solids, nuclei).

### 3.13 Transit-time broadening

A beam of atoms moving with velocity \( \vec{v} = v\hat{x} \) crosses a laser beam propagating along \( \hat{y} \). The cw narrow-band laser beam has frequency \( \omega_L \), its \( z \)-dimensions are greater than those of the atomic beam, and its intensity is \( I(x, z) = I_0 \) for \( -w < x < w \) and zero elsewhere. Assume that the laser light is of sufficiently low intensity so that all saturation effects can be ignored. Also assume that the density of atoms in the beam is low enough so that the atomic beam may be treated as an optically thin medium.

(a) Estimate the broadening of the absorption line due to the finite time of interaction between atoms and the light (transit-time broadening).

(b) Suppose the laser is tuned to a transition between the atomic ground state and an excited state (separated in energy by \( \hbar \omega_0 \)) with radiative lifetime \( \tau \). For \( v = 5 \times 10^4 \) cm/s and diameter \( 2w = 1 \) mm, estimate for which values of \( \tau \) transit-time broadening effect will dominate the line width.

(c) Using a classical and/or quantum mechanical picture, explain the additional lobes on the spectral profile of a transit-broadened line (see Fig. 3.20). Assume that the lifetime of the excited state \( \tau \) greatly exceeds the transit time \( \sim 2w/v \).

(d) What is the spectrum of a transit-broadened line if we instead assume a Gaussian spatial profile for the laser beam, i.e., \( I(x, z) = I_0 e^{-2x^2/w^2} \)? (The factor of 2 appears in the exponent because the beam radius is conventionally defined to correspond to the \( 1/e \) level for the electric field amplitude.)
TRANSIT-TIME BROADENING

Solution

(a) An atom traversing the laser beam “sees” a pulse of radiation with a duration $2w/v$. This means that the effective radiation spectrum is broadened according to the uncertainty condition

$$\Delta \nu \Delta t \sim \frac{1}{2\pi}. \quad (3.238)$$

Therefore,

$$\Delta \nu_{\text{transit}} \sim \frac{v}{4\pi w}. \quad (3.239)$$

(b) For $v = 5 \times 10^4 \text{ cm/s}$ and $2w = 1 \text{ mm}$, this corresponds to

$$\Delta \nu_{\text{transit}} \sim 0.1 \text{ MHz}. \quad (3.240)$$

The radiative width is

$$\Delta \nu_{\text{radiative}} = \frac{1}{2\pi \tau}. \quad (3.241)$$

Therefore, the transit broadening dominates when

$$\tau \gg 2 \mu \text{s}. \quad (3.242)$$

(c) Suppose that the laser light phase is such that its electric field at the atom is $\mathcal{E}(t) = \mathcal{E}_0 \cos(\omega_L t)$. The intensity spectrum of this radiation can be found by

\[ F_{\text{IG}}. ~ 3.20 \]

Absorption spectrum for atomic transition where the lineshape is due to transit-time broadening.
taking the Fourier component:

\[ E(\omega) = \int_{t=-w/v}^{t=w/v} E_0 \cos(\omega_L t') e^{-i\omega t'} \, dt', \] (3.243)

and evaluating the quantity \( I(\omega) \propto E(\omega)E(\omega)^* \). One finds, after some math, that

\[ I(\omega) \propto \sin^2 \left( \frac{(\omega - \omega_L)w/w}{(\omega - \omega_L)^2} \right). \] (3.244)

This function is centered around the laser frequency \( \omega_L \). If one scans the laser light frequency through the atomic resonance, the absorption spectrum [resulting from the spectral intensity distribution (3.244)] is that shown in Fig. 3.20 (in the limit where \( \tau \gg w/v \)).

The lobes on the spectral profile are analogous to those that appear in the diffraction of light from a thin slit. In the case of a thin slit, the properties of a monochromatic field are modified by limiting the extent of the field in space, while in transit-time broadening, the properties of the field are modified by limiting the extent of the field in time.

(d) In this case, the time-dependent electric field seen by atoms passing through the laser beam is given by

\[ E(t) = E_0 \cos(\omega_L t) e^{-v^2t^2/w^2}, \] (3.245)

where we have transformed the spatial dependence of the laser beam intensity into the time-dependence of the electric field by setting \( E(t) = \sqrt{I(x=vt, z)} \). As in part (c), we take the Fourier transform of \( E(t) \):

\[ E(\omega) = \int_{-\infty}^{\infty} E_0 \cos(\omega_L t') e^{-v^2t'^2/w^2} e^{-i\omega t'} \, dt', \] (3.246)

and for \( I(\omega) \propto E(\omega)E(\omega)^* \) we obtain

\[ I(\omega) \propto e^{-w^2(\omega - \omega_L)^2/(2v^2)}, \] (3.247)

where we have ignored far-off resonant terms involving factors of \( \exp[-w^2(\omega + \omega_L)^2/(2v^2)] \). Thus the spectral profile in this case is a Gaussian. Note that the

\[ \text{The Fourier transform or the spectral distribution of an arbitrary time-dependent function } F(t) \text{ is defined as} \]

\[ F(\omega) = \int_{-\infty}^{\infty} F(t) e^{-i\omega t} \, dt. \]

The inverse transformation is

\[ F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} \, d\omega. \]
intensity drops to the $1/e$ point at $|\omega - \omega_L| = \sqrt{2}(v/w)$, whereas the first zeros of the profile shown in Fig. 3.20 occur at $|\omega - \omega_L| = \pi v/w$.

### 3.14 A quiz on fluorescence and light scattering

Here we present a collection of conceptual questions that are designed to test one’s understanding of several key ideas in spontaneous emission and scattering, and help develop intuition in these subjects. In order to minimize possible confusion, we attempt to clearly specify a physical situation to which the question pertains, although the concept illustrated by the question may be of a more general nature. Testing these questions on our colleagues (and ourselves) has convinced us that some of the questions may not be as trivial as might seem at first glance.

(a) A free two-level atom at rest in its ground state is irradiated by a pulse of off-resonant radiation with a Gaussian temporal profile. The light is nearly monochromatic, with spectral width limited by the finite duration of the pulse. The light frequency detuning from resonance greatly exceeds both the radiative width of the upper state and the inverse duration of the light pulse. The excitation light can be considered arbitrarily weak. A photodetector detects photons scattered in a direction not along the direction of excitation light propagation.

Suppose that with the set up described above, it is found that the probability of detecting a scattered photon is $P$. How would this probability change if instead of a single atom we had two? Assume that the atoms are initially localized to a spatial region with linear dimensions much smaller than the reduced wavelength of the light $\lambda/2\pi$. (The initial localization is the same as for the case of one atom.) Assume that for the excitation pulse duration $\tau$, we have:

$$\tau \ll \frac{M c \Delta x}{\hbar \omega},$$

(3.248)

where $M$ is the mass of an atom, $\Delta x$ is its initial localization, and that the two atoms do not interact with each other in the absence of light. What if we have $N$ atoms?

(b) $N \gg 1$ atoms are prepared as above, except they are all in the excited rather than the ground state. No light pulse is applied. How does the radiative decay time depend on $N$?

(c) $N$ atoms are prepared as above, in the ground state; one atom in the excited state is added to the system. No excitation pulse is applied. How does the presence of the $N$ ground state atoms affect the decay?
(d) \(N\) atoms are prepared as above, in the ground state. A single resonant photon is sent into the sample and absorbed, creating one excitation among our \(N\) atoms. How does the radiative decay time for this excitation depend on \(N\)?

(e) Same as (a), but the atoms are now three-level systems, and the detector is equipped with a color filter, so it is only sensitive to light resulting from Raman scattering into the third level.

(f) In the parts above we have assumed that the \(N\) atoms are prepared at zero temperature so their initial motion is only due to spatial localization. How would these results change for atoms of finite temperature? Assume that the excitation pulse is still much shorter than the inverse Doppler width of the transition.

(g) In the parts above we have assumed that the \(N\) atoms are free. What if they are confined in a trapping potential? Assume that the energies of the internal excitations (the upper and the third level) greatly exceed the energy associated with the confining potential.

(h) Weak resonant monochromatic light is scattered in a direction other than forward by a single two-level atom (scattering and resonance fluorescence are the same process in this case). Is the scattered radiation coherent with the input radiation? In other words, is it possible to observe steady interference fringes by combining the scattered light and a portion of the input light, for example, on a distant screen? Neglect atomic recoil.

Solution

(a) The probability of detecting a scattered photon is four times larger in the case of two atoms (or \(\propto N^2\) in general). With the conditions specified in the question, it is impossible, even in principle, to determine which of the two atoms scattered a photon, and thus the amplitudes for scattering on the two atoms interfere constructively. The condition (3.248) is specified so that the Doppler broadening that arises due to atomic motion (cf., for example, Problem 8.1) which is, in turn, due to the atoms’ initial localization, is much smaller than the spectral width of the exciting and scattered light. Note also that the initial localization of atoms in a volume with linear dimensions smaller than the wavelength ensures that the initial momentum uncertainty (\(\sim h/\Delta x\)) exceeds the momentum kick due to photon scattering (\(\sim h\omega/c\)), and thus, it is impossible to say which atom scattered a photon based on its momentum after scattering.

(b) The questions (b) and (c) were originally formulated and answered in a seminal paper by R. H. Dicke (1954), which forms the basis of an entire subfield of modern optics and spectroscopy [see, for example, the monograph by Andreev et al. (1993)].
A QUIZ ON FLUORESCENCE AND LIGHT SCATTERING

The answer to question (b) is that the excited state radiative lifetime will be \( \approx \tau_0/N \), where \( \tau_0 \) is the radiative lifetime of an isolated atom. This is a cooperative emission effect that is known as Dicke superradiance. Its origin can be understood in the following qualitative way. At first, after the atoms have been prepared in the excited state, they “do not know” about each other, and their spontaneous emission proceeds independently. Because we have \( N \) atoms, the first fluorescent photon appears after a characteristic time \( \tau_0/N \). Because the photon is produced where all the atoms are localized, and the atom-photon interaction cross-section is \( \lambda^2/2\pi \) (see Problem 3.5), the first photon interacts with the system of atoms, causing the individual atomic dipoles to phase in,\(^{14}\) thus inducing an “avalanche,” which depletes the upper state population nearly instantaneously.

Note that since the number of emitted fluorescence photons is \( N \), and the emission time is \( \approx \tau_0/N \), the emission intensity is \( \approx N^2 \) that of a single isolated atom.\(^{15}\) A calculation \( \text{[see Andreev et al. (1993), Sargent et al. (1977), and Allen and Eberly (1987)]} \) shows that the peak intensity is \( N^2/4 \) of the single-atom intensity for \( N \gg 1 \).

(c) The presence of the ground state atoms affects the decay in an essential way: while the initial transition probability is the same as for a free excited atom, the overall probability of emitting a photon is \( 1/N \). This means that the radiation is mostly “trapped” within the medium for \( N \gg 1 \). How can it be that one atom in the system is excited (we do not know which one because the atoms exchange their excitations through the electromagnetic field) but the system never radiates? Actually, this is a purely classical effect. Assume there are two co-located identical classical dipoles that can only lose their energy through radiation. There are two modes of the system’s oscillation: the symmetric mode where the two dipoles oscillate in phase, and the antisymmetric mode where they oscillate with a phase shift of \( \pi \). Clearly, the energy is radiated in the symmetric mode but there is no radiation at all for the antisymmetric mode. If a system is prepared with one dipole initially excited (i.e., a superposition of the symmetric and antisymmetric mode), half of the energy is radiated, while the remaining energy is stored in the antisymmetric collective oscillation of the two dipoles. For the case of \( N \) oscillators, the

\(^{14}\) Detailed theoretical treatments (Andreev et al. 1993) make a distinction between the interactions between the atoms through the radiation field that establish collective emission and stimulated emission.

\(^{15}\) Here we assume that the spectral width of the emitted radiation \( \approx N/\tau_0 \) is much smaller than the transition frequency. Also, because pulse shortening due to collective emission leads to spectral broadening, one may wonder how the energy balance is preserved. The explanation lies in the fact that the initial state has to be prepared in a short time compared to the emission time, for example, with a short pulse of radiation bringing each atom from the ground to the excited state (such an inverting pulse is called a “\( \pi \)-pulse.”) Because this pulse is short, there is inevitably an uncertainty in the energy of its photons, so there is no problem with the overall energy balance.
solution of the classical problem [see, for example, Andreev et al. (1993)] shows that \( N - 1 \) out of the total \( N \) modes do not radiate.

The quantum mechanical treatment developed by Dicke (1954) uses the notion of the collective pseudospin for the ensemble of \( N \) two-level atoms. The analogy with the real spin becomes obvious if instead of free two-level atoms, one thinks of spin-1/2 particles with magnetic moments placed in a uniform magnetic field (Allen and Eberly 1987). \( N \) atoms, all in the ground state, correspond to a symmetric wavefunction with the pseudospin projection \(-N/2\), while \( N \) atoms, all in the excited state, correspond to a symmetric wavefunction with the pseudospin projection \( N/2 \). Clearly, both these wavefunctions correspond to the total pseudospin of the system of \( N/2 \). It is straightforward to show that dipole transitions are only possible between states of the same total pseudospin. This has an immediate consequence that out of the total \( N \) possible states with a single excited atom, only one (the totally symmetric state) can decay to the ground state with no atomic excitations. This is analogous to the classical result discussed above.

We have explained why the overall probability of the photon emission is \( 1/N \).

In part (d), we will show that the only state with a single excitation that can radiate, the symmetric state, has a dipole moment coupling it to the ground state which is \( \sqrt{N} \) times larger than that for a single atom. Thus the symmetric state with a single excitation radiates with \( N \) times higher intensity than a single excited atom. Since the weight of this state in the initial state is \( 1/N \), the total initial intensity is the same as for an isolated excited atom. On the other hand, since the total radiated energy is \( N \) times smaller, this also means that the characteristic emission time is \( \tau_0/N \).

(d) Each of the atoms in our sample upon absorption of the photon is prepared in a coherent superposition of the ground and excited states. The amplitude of the excited state in this superposition is \( 1/\sqrt{N} \), so that summing the probability of finding the atoms in the excited state over all atoms we get one.

A coherent superposition of the upper and lower atomic states corresponds to a dipole moment (in this case, of amplitude \( 1/\sqrt{N} \) of its maximum value) oscillating at the frequency of the transition. We have \( N \) such dipoles that oscillate coherently. Adding all the amplitudes and squaring, we get \((N \cdot 1/\sqrt{N})^2 = N \). Thus the intensity of the emission is enhanced by a factor of \( N \) compared to the case of an isolated atom, and the radiative decay time is decreased by \( N \).

(e) In this case, the scattering probability scales linearly with the number of atoms. Since the scattering process leaves an atom in a state different from its initial state, it is possible to tell exactly which atom scattered the light by doing an additional measurement after the fact. Thus, scattering amplitudes involving different atoms do not interfere.
(f) None of the results above change for atoms of finite temperature assuming that the excitation pulse is much shorter than the inverse Doppler width of the transition. We note that in recent years, quantum degenerate atomic vapors, and in particular, Bose-Einstein condensates, became a new laboratory for experimental investigation of collective emission and scattering processes, as reviewed by Ketterle and Inouye (2001).

(g) The atoms occupy the energy levels of the confining potential, not necessarily one and the same level.\(^\text{16}\) The Doppler width considerations are irrelevant in the case of a sufficiently strong potential, but the previous results remain valid if an atom scattering a photon is most likely to remain in the same energy level of the potential upon scattering [so that we still cannot tell which atom scattered the photon, except for the case of part (c)]. The condition for this is that the recoil energy for an isolated atom is much smaller than the interval between adjacent energy levels of the trapping potential. This is completely analogous to the Mössbauer effect — the absence of recoil in nuclear emission/absorption of gamma rays when the emitter and absorber are part of a crystalline lattice [see, for example, Wertheim (1964)].

(h) The scattered light is indeed coherent with the excitation light, i.e. their relative phase is not random. This can be understood from the fact that the scattered radiation is produced by the atomic dipole (corresponding to a superposition of the ground and excited states) whose oscillation frequency and phase are determined by the driving field. This is in contrast to the spontaneous emission for an atom initially prepared in the excited state, for which the phase of the emitted light is random. A detailed discussion of coherence properties of scattered and resonance fluorescence light is given in Chapter 8 of the book by Loudon (2000).

### 3.15 Two-photon transition probability

Consider the system of energy levels shown in Figure 3.21. Estimate the two-photon transition probability for excitation of atoms from state \(|i\rangle\) to state \(|f\rangle\) upon the action of two light fields of frequencies \(\omega_1, \omega_2\). Assume that the \(|i\rangle \rightarrow |k\rangle\) and \(|k\rangle \rightarrow |f\rangle\) transitions are electric-dipole (\(E1\)) allowed with transition moments \(d_{ik}\) and \(d_{kf}\), respectively. Neglect Doppler broadening, and assume the condition of two-photon resonance:

\[
\hbar \omega_1 + \hbar \omega_2 = E_f - E_i. \tag{3.249}
\]

In general, two-photon transitions arise in second-order perturbation theory, with the electric field of the light as the perturbation. Their amplitude contains

\(^{16}\) The maximum occupation number depends on whether the atoms are fermions or bosons.
FIG. 3.21 Energy levels involved in a two-photon transition. Cases (a) and (b) differ by the order of absorption of photons with frequencies $\omega_1$, $\omega_2$.

two terms, which are different in the order of absorption of the $\omega_1$ and $\omega_2$ photons [Figures 3.21(a) and (b)]. For simplicity, let us consider the case where

$$|\hbar \omega_1 - (E_k - E_i)| \ll |\hbar \omega_2 - (E_k - E_i)|,$$  \hspace{1cm} (3.250)

so the term with an $\omega_1$ photon absorbed first [Figure 3.21(a)] dominates over the term where it is an $\omega_2$ photon that is absorbed first [Figure 3.21(b)]. Also, we assume that for single-photon detuning $\Delta \equiv \hbar \omega_1 - (E_k - E_i) = E_f - E_k - \hbar \omega_2$, we have $|\Delta| \gg \Gamma_k$, where $\Gamma_k$ is the natural width of the intermediate level.

Solution

If only the first light field is present, the atoms undergo Rabi oscillations with frequency

$$\Omega_1 = \sqrt{\Delta^2 + \frac{d_{ik} E_1^2}{\hbar^2}},$$  \hspace{1cm} (3.251)

and the maximal amplitude of finding atoms in the state $|k\rangle$ is $d_{ik} E_1 / (\hbar \Omega_1)$ (see Problem 3.1). Here $E_1$ is the electric field amplitude of the $\omega_1$ light. Therefore the time averaged probability $\langle P_k \rangle$ to find an atom in $|k\rangle$ is

$$\langle P_k \rangle = \frac{1}{2} \frac{d_{ik} E_1^2}{\hbar^2 \Omega_1^2}.$$  \hspace{1cm} (3.252)

Since now there is nonzero amplitude to find the atom in state $|k\rangle$, there appears the possibility for an atom to absorb an $\omega_2$ photon and go to the state $|f\rangle$.

It is interesting to abandon for a moment the two-photon resonance condition (3.249) and discuss the absorption spectrum of such a system with respect to tuning of $\omega_2$. From energy conservation, it is clear that there is absorption only when the condition (3.249) is satisfied (to within the transition linewidth); otherwise,
there is no absorption (including for \( h\omega_2 = E_f - E_k \)), since then there would be an imbalance between the energy of the two absorbed photons and the energy of atomic excitation. It is often said that in the presence of the field \( \omega_1 \) a virtual state is excited (dashed lines in Figure 3.21), which is essentially state \( |k\rangle \), except its energy is \( E_i + h\omega_1 \).

According to this picture, we can consider the next stage of the excitation process as a single photon transition from the resonant virtual state to \( |f\rangle \). Assuming that the Rabi frequency for this second stage is much smaller than the natural width of the final state \( \Gamma_f \) (so that the system is in the overdamped regime, see Problem 3.1), the transition rate (the number of two-photon absorption events per atom per unit time) is given by

\[
W_{2\gamma} \approx \langle P_k \rangle \frac{d^2_{kf}E_2^2}{\hbar^2\Gamma_f} \approx \frac{1}{2} \frac{1}{\hbar^2\Gamma_f} \left[ \frac{(d_{ik}E_1d_{kf}E_2)^2}{\Delta^2 + (d_{ik}E_1/h)^2} \right].
\]

(3.253)

(The factor of 1/2 comes from the time-averaged population of the intermediate state \([\text{Eq. (3.252)}]\).)

This expression shows that when both light fields are weak, the two-photon transition rate scales as the product of their intensities. For high intensity of the \( \omega_1 \) light such that \( (d_{ik}E_1)^2 \gg \Delta^2 \), the transition rate becomes independent of the intensity of this field (saturation). Although formula (3.253) does not show saturation for strong \( \omega_2 \) light, this is a consequence of an implicit assumption that we made in the derivation: namely, that the \( \omega_2 \) field is sufficiently weak as not to affect the evolution of the two-level system consisting of states \( |i\rangle \) and \( |k\rangle \) in the presence of the \( \omega_1 \) field. A detailed calculation that does not rely on this assumption (Ter-Mikaelyan 1997) shows that in fact the two-photon transition rate as a function of the \( \omega_2 \) intensity (for a given weak \( \omega_1 \) field) also saturates when \( (d_{kf}E_2)^2 \gg \Delta^2 \). It is interesting to note that when one of the fields \( \omega_1, \omega_2 \) is weak, the two-photon transition rate cannot exceed the resonant single-photon transition rate corresponding to the weak field, no matter how strong the other field is.

Various other aspects of two-photon transitions are discussed by, for example, Krainov et al. (1997).

### 3.16 Vanishing Raman scattering

*Raman scattering* is a process in which a photon is removed from the incident light beam, and a photon of a different frequency is emitted. The atoms or molecules of the Raman medium are transferred to states other than the initial one in the process of scattering. Consider Raman scattering for a model energy level system
shown in the absorption-emission diagram of Fig. 3.22. Using the Feynman diagram technique (Appendix H), write down the amplitude of the process. Show that this amplitude vanishes when the energy of the “$2P$” level is exactly in the middle between the energies of “$2S$” and “$1S$.” The electric dipole transition amplitude between $1S$ and $2S$ is zero.

Solution

The two possible Feynman diagrams (see Appendix H) for this process are shown in Fig. 3.23. The overall amplitude of the process is therefore

$$V_{1S \rightarrow 2S} \propto \frac{d_{21} d_{22}}{E_{2P} - \hbar \omega_1} + \frac{d_{21} d_{22}}{(E_{2P} + \hbar \omega_1 + \hbar \omega_2) - \hbar \omega_1}, \quad (3.254)$$

**Fig. 3.22** Raman scattering in a model system.

**Fig. 3.23** Feynman diagrams corresponding to the process depicted in Fig. 3.22.
where we set $E_{1S} = 0$ and $d_{mn}$ designates the corresponding dipole amplitude. Energy conservation requires $\hbar(\omega_1 - \omega_2) = E_{2S}$. With this, it is immediately seen from Eq. (3.254) that the amplitude vanishes when $E_{2S} = 2E_2P$.

Note that when $\omega_1$ is much greater than the energy level splittings between the $1S$, $2S$, and $2P$ levels, all energy differences between the levels are effectively zero. Thus Raman scattering also vanishes in the high frequency limit.

### 3.17 Excitation of atoms by off-resonant laser pulses

Consider two-level atoms (originally in state $|1\rangle$) interacting with an off-resonant laser pulse (Fig. 3.24). Suppose that the temporal profile of the pulse is Gaussian with full width at half maximum (FWHM) of $\tau$. Suppose further that the light, although it is near resonant, is well-detuned from the resonance so that $\Delta \gg 1/\tau$, where $\Delta$ is the detuning. Assume also that $\tau \ll 1/\Gamma$, where $\Gamma$ is the total radiative width of the upper state.

(a) Assuming weak intensity of the light, estimate the probability of finding atoms in state $|2\rangle$ after the pulse is essentially over but the state $|2\rangle$ has not had time to decay via spontaneous emission. Discuss the dependence of this probability on $\Delta$. The partial width for the $|2\rangle \rightarrow |1\rangle$ decay is $\Gamma_p$.

(b) Discuss power broadening (see Problem 3.7) of the excitation spectral profile. (In other words, how does the excitation line width scale with light power at high powers?)
Note: This problem is based on the results of Makarov (1983); see also Letokhov (1987), Chapter 2.

Solution

(a) Although atoms may undergo absorption-emission cycles while the light pulse is on, they should always return to the initial state after the pulse is over if we only consider one- and two-photon processes. A two-photon process must return the system to its original state in this two-level approximation, while a process where a photon is absorbed from the laser beam and the atom remains in the upper state after the pulse is over is forbidden by energy conservation. This is an example of adiabatic evolution where the system follows the quantum state as it evolves under a time-dependent perturbation, and thus returns to the initial state after the perturbation subsides.

A nonzero excitation probability arises in the next order of perturbation theory, i.e., we need to consider a three-photon process: two laser photons are absorbed, and one photon is spontaneously emitted. Because the energy of the spontaneously emitted photon is not restricted to coincide with the frequency of the laser light, the three-photon process could be exactly resonant (or, more precisely, resonant within the width $\Gamma$), which allows the system to satisfy energy conservation, or, in other words, removes the condition of adiabaticity of the process.

Possible Feynman diagrams (see Appendix H) for a three-photon process where two laser photons ($\omega_l$) are absorbed and one photon ($\omega_s$) is spontaneously emitted are shown in Fig. 3.25. Of these diagrams, the diagram C is the most important because of the resonant enhancement of the corresponding amplitude:

$$V_{21} \approx V_{21}(C) \sim \frac{d_2 E_l^2 E_s}{\hbar^2 \Delta^2}.$$  \hspace{1cm} (3.255)

Equation (3.255) shows that the probability of finding atoms in state $|2\rangle$ scales as $\Delta^{-4}$ with respect to detuning. This should be contrasted, for example, with the more familiar Lorentzian line shape that gives a transition probability in the case of continuous wave monochromatic excitation whose wings drop as $\Delta^{-2}$.

The probability of finding atoms in state $|2\rangle$ after the laser pulse can be calculated from the amplitude of Eq. (3.255) as discussed in Appendix H. Instead, we estimate this probability from the following qualitative argument.

We can view the excitation to the upper state $|2\rangle$ as a three-stage process. First, the atom begins in state $|1\rangle$, the laser pulse smoothly “turns on,” and the atom now has a probability $d_2 E_l^2 / (\Delta^2)$ of being in the upper state (see Problem 3.1). However, if no spontaneous emission occurs during the pulse, the atom will adiabatically return to $|1\rangle$ once the pulse smoothly turns off.

17 We also neglect processes where, for example, an $M1$ spontaneous photon is emitted.
Feynman diagrams corresponding to three-photon processes where two laser photons are absorbed and one photon is spontaneously emitted. The diagram C is resonantly enhanced with respect to the diagrams A and B.

Thus we require a second stage: spontaneous emission from $|2\rangle$ back to $|1\rangle$ during the pulse to break the adiabaticity condition. The probability $P_{\text{spont}}$ for such a spontaneous emission event is the product of the population of $|2\rangle$ during the pulse, the spontaneous decay rate $\Gamma_p$, and the duration of the pulse:

$$P_{\text{spont}} \approx \frac{d^2 E_l^2}{2\Delta^2} \Gamma_p \tau.$$  \hspace{1cm} (3.256)

If such an event occurs, at this instant the atom is reset to state $|1\rangle$ while the light field is still on.
Finally, the third stage is excitation back to $|2\rangle$, but in such a way that the atom remains in $|2\rangle$ after the pulse is smoothly turned off. An important point regarding this third stage is that the perturbation trying to excite the atom to $|2\rangle$ has a temporal profile that looks like the sketch in Fig. 3.26. Because the perturbation appears to be “suddenly” switched on, the probability to end up in the excited state is $\sim d^2E_l^2/(2\Delta^2)$. One way to see this: the perturbation being suddenly turned on is equivalent to the pulse being suddenly turned off (for which the answer is more obvious).

Combining all these factors, we get for the probability

$$ P(1 \rightarrow 2) \sim \frac{d^4E_l^4}{2\hbar^4\Delta^4\Gamma_p\tau}. $$

(b) Power broadening occurs when $dE_l$ becomes comparable to $\hbar\Delta$, and thus the latter is no longer the largest relevant energy scale in the problem. With a given value of $dE_l$, the detuning $\Delta^*$ beyond which the probability of finding atoms in state $|2\rangle$ is described by Eq. (3.257) is thus given by $\Delta^* \sim dE_l/\hbar$, i.e. the spectral width of the resonance scales as the square root of the pulse intensity, the usual scaling for power-broadened resonances [see Problem 3.7, Eq. (3.173)].

### 3.18 Hyperfine-interaction-induced magnetic dipole (M1) transitions

Consider one-photon transitions between $nS_{1/2}$ and $n'S_{1/2}$ states of the same parity ($n$, $n'$ are the principal quantum numbers; $n \neq n'$) in an atom with a single
HYPERFINE-INTERACTION-INDUCED MAGNETIC DIPOLE (M1) TRANSITIONS

$s$-electron above the closed shells, for example, the $6S_{1/2} \rightarrow 7S_{1/2}$ transition originating from the ground state of Cs. The parity selection rule forbids this transition from proceeding as $E1$; the magnetic ($M1$) amplitude turns out to be strongly suppressed as well. In fact, the magnetic dipole Hamiltonian is given by (see, for example, Problem 1.4):

$$H_{M1} = -\vec{\mu} \cdot \vec{B} = \mu_0 (\vec{l} + 2\vec{s}) \vec{B},$$  \hspace{1cm} (3.258)

where $\vec{\mu}$ is the magnetic moment operator, $\vec{B}$ is the magnetic field of the light, and $\vec{l}$ and $\vec{s}$ are the orbital and spin angular momentum operators, respectively (note that $\vec{l}$ does not contribute for $S \rightarrow S$ transitions, so this term will be ignored in the subsequent discussion). The matrix element of the operator $H_{M1}$ between states with different principal quantum numbers is identically zero because the angular momentum operators do not affect the radial wavefunctions, and radial wavefunctions are orthogonal for states with different principal quantum numbers. A nonzero contribution to the $M1$ amplitude on the order of $10^{-4} \mu_0$ arises from configuration mixing of the $6S_{1/2}$ and $7S_{1/2}$ states with states that have electrons excited from the closed shells [see, for example, Khriplovich (1991), Chapter 5.1], the evaluation of which requires complicated atomic calculations. In this problem, we are concerned with another, nuclear spin-dependent contribution to the $M1$ amplitude of comparable magnitude which arises due to off-diagonal hyperfine interactions (Problem 1.11).

Show that the hyperfine-interaction-induced $M1$ amplitude can be related to the hyperfine splittings $\Delta E_{hf}$ in the upper and the lower state (which can be precisely measured) according to (Hoffnagle 1982):

$$\langle \tilde{n}'S_{1/2}F'M'|\tilde{\mu}|\tilde{n}S_{1/2}FM \rangle = 2\mu_0 \sqrt{\Delta E_{hf}} \Delta E_{hf} \left( F - F' \right) \langle F'M'|\vec{s}|FM \rangle,$$

where the tildes designate hyperfine-interaction-mixed states.

This effect turns out to be important in experiments measuring parity-violation in alkali atoms such as Cs (Problem 1.13).

**Solution**

In the case of $s$-electrons, the hyperfine interaction between the magnetic moments of the nucleus and the electron is of contact character (the Fermi contact interaction) whose Hamiltonian can be written as (Problem 1.4):

$$H_{hf} = c\delta(r) \vec{I} \cdot \vec{s},$$  \hspace{1cm} (3.260)

where $c$ is a constant, $\delta(r)$ is the $\delta$-function, and $\vec{I}$ is the nuclear spin operator. The Hamiltonian (3.260) is a scalar operator with respect to atomic wavefunctions.
(Appendix F), and thus mixes only states of the same total angular momentum \( F \) and its projection \( M \) (and also, in general, with the same quantum numbers \( L \) and \( S \), but not necessarily \( J \), see Problem 1.11):

\[
\langle \tilde{n} S_{1/2} F M | \tilde{\mu} | \tilde{n} S_{1/2} F' M' \rangle = a_{\text{off}} \frac{F(F+1) - I(I+1) - s(s+1)}{E_n - E_{n'}} \langle n' S_{1/2} F M' \rangle ,
\]

(3.261)

\[
\langle \tilde{n} S_{1/2} F' M' | \tilde{\mu} | \tilde{n} S_{1/2} F M \rangle = a_{\text{off}} \frac{F'(F'+1) - I(I+1) - s(s+1)}{E_{n'} - E_n} \langle n S_{1/2} F' M' \rangle.
\]

(3.262)

In Eqs. (3.262) and (3.263),

\[
a_{\text{off}} = c \psi_n(0) \psi_{n'}(0),
\]

(3.264)

where \( \psi_n, \psi_{n'} \) are the real wavefunctions of the corresponding \( s \)-states. The matrix element of \( \vec{\mu} = -2 \mu_0 \vec{s} \) between the states (3.262) and (3.263) is then:

\[
\langle \tilde{n} S_{1/2} F' M' | \vec{\mu} | \tilde{n} S_{1/2} F M \rangle = a_{\text{off}} \frac{F(F+1) - F'(F'+1)}{E_n - E_{n'}} \langle F' M' | \vec{s} | F M \rangle,
\]

(3.265)

where we used the independence of the matrix elements of \( \vec{s} \) of the principal quantum number. Note that the \( M1 \) amplitude (3.265) vanishes for \( F' = F \). Since \( l = 0 \), there are only two possibilities for having \( F' \neq F \):

- \( F' = I + 1/2; F = I - 1/2; F' - F = 1 \), and
- \( F' = I - 1/2; F = I + 1/2; F' - F = -1 \).

In either case, we have:

\[
F(F+1) - F'(F'+1) = (F - F')(2I + 1).
\]

(3.266)

The remaining step in deriving Eq. (3.259) is to relate \( a_{\text{off}} \) to the hyperfine structure splittings. Using the Hamiltonian (3.260), we find for the hyperfine shift
of the levels:

\[
E_{hf}^n(F) = \langle nF | c \delta(r) \vec{I} \cdot \vec{s} | nF \rangle = c \psi_n^2(0) \frac{F(F + 1) - I(I + 1) - s(s + 1)}{2},
\]

from which we have:

\[
\Delta E_{hf}^n = E_{hf}^n(F = I + 1/2) - E_{hf}^n(F = I - 1/2) = c \psi_n^2(0)(I + 1/2),
\]

and similarly for \( n', F' \). From this and Eq. (3.264), it follows that

\[
a_{\text{off}} = \frac{\sqrt{\Delta E_{hf}^n \Delta E_{hf}^{n'}}}{I + 1/2},
\]

which, upon substitution into Eq. (3.265) together with Eq. (3.266), yields the sought-for Eq. (3.259).

### 3.19 Transitions with unresolved hyperfine structure

Consider an atomic transition between states with total electronic angular momentum \( J \) and \( J' \) respectively, where \( J = 1/2 \) and \( J' = 1/2 \). The nucleus of the atom has spin \( I = 1/2 \). The initial and the excited state each have two hyperfine components with total angular momenta \( F \) (or \( F' \)) = 0 and \( F \) (or \( F' \)) = 1. We prepare the initial state such that its wavefunction is

\[
|\psi(0)\rangle = \frac{|F = 1, M = 1\rangle + |F = 1, M = -1\rangle}{\sqrt{2}},
\]

and measure absorption of linearly polarized light [e.g., \( (\sigma_+ + \sigma_-)/\sqrt{2} \)] propagating along the quantization axis (\( \hat{z} \)). Later on, as a result of, for example, Larmor precession in a magnetic field applied along \( \hat{z} \), the wavefunction of the initial state evolves into

\[
|\psi(t)\rangle = \frac{|F = 1, M = 1\rangle - |F = 1, M = -1\rangle}{\sqrt{2}}
\]

at time \( t \). Note that the evolution from \( |\psi(0)\rangle \) to \( |\psi(t)\rangle \) corresponds to Larmor precession by \( \pi/2 \) (here we neglect any overall phase factor which is not important for the present considerations).

(a) Assuming an electric-dipole (E1) transition where all hyperfine levels are spectrally resolved, calculate the relative absorption coefficients for light tuned to each of the possible hyperfine-structure transitions. Compare these coefficients for the initial state being \( |\psi(0)\rangle \) and \( |\psi(t)\rangle \).
(b) Compare the absorption coefficients for the initial state being $|\psi(0)\rangle$ and $|\psi(t)\rangle$ for the case of light that is sufficiently broadband so that the upper-state hyperfine structure is unresolved.

(c) Give a qualitative explanation of the result of part (b). Formulate a general theorem concerning light absorption from a polarized state when the final-state hyperfine structure is unresolved.

**Hint**

To solve this problem, it may be useful to employ the results of Problem 3.4 and the fact that the reduced dipole matrix element for a transition between hyperfine-structure levels can be found according to [see, for example, Appendix I and the book by Sobelman (1992), Sections 4.3.5 and 9.2.3]:

$$\langle e, I, J', F' || d || g, I, J, F \rangle = (-1)^{J+1+J'+F'} \langle e, J' || d || g, J \rangle \sqrt{(2F'+1)(2F+1)} \left\{ \begin{array}{ccc} J' & F' & I \\ F & J & 1 \end{array} \right\}. \quad (3.272)$$

This result can be derived by expanding the initial and final states into the $|J, M_J\rangle |I, M_I\rangle$ basis and applying rules for summation of combinations of the angular coefficients. Of course, the present problem can also be solved by applying the Clebsch-Gordan expansion without explicitly using the result (3.272).

**Solution**

(a) From Eqs. (3.272) and (3.132),

$$W_{eg} = \frac{1}{\gamma} \frac{\langle \langle e, J' || d || g, J \rangle \rangle^2 E_0^2}{\hbar^2} \frac{\langle J, M_J, 1, 0 || J', M'_J \rangle^2}{2J'+1},$$

we find the following relative absorption rates:

- $|\psi(0)\rangle$:
  - $F = 1 \rightarrow F' = 0$, $W \propto 2/3$,
  - $F = 1 \rightarrow F' = 1$, $W \propto 0$.

- $|\psi(t)\rangle$:
  - $F = 1 \rightarrow F' = 0$, $W \propto 0$,
  - $F = 1 \rightarrow F' = 1$, $W \propto 2/3$.

Note that for the given choice of light polarization, $|\psi(0)\rangle$ is a dark state for the $1 \rightarrow 1$ transition and $|\psi(t)\rangle$ is a dark state for the $1 \rightarrow 0$ transition.
If the final-state hyperfine structure is unresolved, in order to find the total absorption rate, we need to add the absorption rates for the $1 \to 1$ and $1 \to 0$ transitions. We see that, in this case, the absorption does not change when the wavefunction is rotated by $\pi/2$ around the quantization axis. In fact, it is also straightforward to see from this result that the absorption rate is invariant with respect to an arbitrary rotation of the initial state around $\hat{z}$.

The reason that absorption is invariant with respect to rotations of the atomic state when hyperfine structure is not resolved is that the total electronic angular momentum of the initial state is $J = 1/2$ and such a state cannot support polarization moments (Problem 9.7 and Appendix G) with rank $\kappa$ higher than $2J = 1$. The polarization moments corresponding to the states $|\psi(0)\rangle$ and $|\psi(t)\rangle$ are of rank $\kappa = 0$ (population) and $\kappa = 2$ (alignment). When hyperfine structure is not resolved, we can neglect the nuclear-spin part of the wavefunction. However, since the electronic state cannot support alignment, it is impossible to detect the alignment of the initial state using light absorption.

The general theorem can be formulated as follows. Suppose we have a state with electronic angular momentum $J$, nuclear spin $I$ and total angular momentum $F$. We prepare any kind of polarization in this state and want to probe it using weak probe light tuned to a transition to some other state with $J'$, for which the hyperfine structure is unresolved. Then, the signal is only sensitive to the initial-state polarization moments of rank $0 \leq \kappa \leq \min\{2, 2J\}$. Here we have taken into account the fact that one-photon transitions are insensitive to polarization moments with $\kappa$ greater than 2 (alignment) because photons have spin 1. In order to detect polarization moments of rank $\kappa$, the atomic states involved in the transition as well as the light field must be able to support polarization moments of rank $\kappa$.

Because the spatial symmetry of an angular-momentum state is directly related to polarization moments (Problem 9.7), there is a consequence of the theorem for Zeeman beats. In general, if an atom is undergoing Larmor precession in a magnetic field, in the probe signal, one can observe contributions (beats) at the Larmor frequency (due to orientation) and twice the Larmor frequency (due to alignment). However, when the final-state hyperfine structure is unresolved, no beats can be observed for $J = 0$ states and only beats at the Larmor frequency (but not twice the Larmor frequency) can be observed for $J = 1/2$ states.

### 3.20 Optical pumping and quantum beats in Mercury

This problem will provide an illustration of how nuclear spins can be optically polarized, even if the transitions’ hyperfine structure is not spectrally resolved. It will also provide a nice demonstration of the phenomenon of hyperfine quantum beats [see Haroche (1976), for example]. Quantum beats occur when an atom is
put into a superposition of different eigenstates of the atomic Hamiltonian with distinct energies. In such a situation, light interacting with the atom exhibits oscillatory behavior at the frequency corresponding to the energy splitting between the eigenstates. The oscillatory behavior can be observed, for example, in the intensity of fluorescence emitted in a particular direction or in the polarization of light absorbed or emitted.

The ground state of the mercury atom has total electronic angular momentum \( J = 0 \), while the nuclear spin for \(^{199}\text{Hg}\) is \( I = 1/2 \). Suppose we initially have unpolarized atoms, and we apply a short pulse of circularly polarized light tuned to resonance with a transition to an excited \( J' = 1 \) state.

(a) What are the hyperfine-structure levels in the ground and the excited state?

(b) What is the nuclear polarization (the average projection of the nuclear spin on the direction of the circular polarization of the light) right after the excitation pulse? Give a qualitative explanation to this result.

(c) What is the nuclear polarization as a function of time?

(d) Explain how the results above pertain to optical pumping of nuclear spins. In parts (b)-(c), only consider the atoms in the excited electronic state.

Solution

(a) The hyperfine structure of the states involved is shown in Fig. 3.27 along with the laser-induced transitions. Obviously, there is no hyperfine splitting in the ground state because \( J = 0 \).

(b) Before the excitation pulse, we have an unpolarized ground state, i.e., an incoherent mixture of the ground state Zeeman sublevels. With left-circularly polarized light, the atoms in the \( |F = 1/2, M_F = 1/2\rangle \) sublevel can only be excited to the \( |F' = 3/2, M_{F'} = 3/2\rangle \) sublevel, which is an eigenstate of the Hamiltonian for the atom. Therefore, upon excitation, there are no quantum beats associated with this state since the atom is not in a superposition state. Note that the polarization of the nucleus is not affected by the transition – the nucleus is just a “spectator” to the process.

Let us now consider the fate of the atoms that are initially in the \( |F = 1/2, M_F = -1/2\rangle \) sublevel. Such atoms are coherently excited to a superposition of \( |F' = 3/2, M_{F'} = 1/2\rangle \) and \( |F' = 1/2, M_{F'} = 1/2\rangle \). Let us evaluate the corresponding amplitudes in terms of the reduced matrix element of the transition \( \langle J' || d || J \rangle \). To do this, we find the values of the reduced matrix elements \( \langle F' || d || F \rangle \)
according to Eq. (3.272) (see Problem 3.19),
\[
\langle (J' I) F' || d || (JI) F \rangle = (-1)^{J' + I + F + 1} \sqrt{(2F' + 1)(2F'' + 1)} \begin{pmatrix} J' & F' & I & 1 \end{pmatrix} \langle J' || d || J \rangle,
\]
which are $-\sqrt{2}\langle J' || d || J \rangle / 3$ for the case of $F' = 1/2$ and $2\langle J' || d || J \rangle / 3$ for the case of $F' = 3/2$. Using the Wigner-Eckart theorem [see Appendix F and Appendix I, Eq. (I.18)]
\[
\langle F' M_F' | d_q \rangle | F M_F \rangle = (-1)^{F' - M_F'} \begin{pmatrix} F' & 1 & F \end{pmatrix} \begin{pmatrix} -M_F' & q & M_F \end{pmatrix} \langle F' || d || F \rangle,
\]
we find that the following superposition of the $M_F' = 1/2$ states is excited from the $F = 1/2, M_F = -1/2$ state (see Problem 3.4):
\[
|\psi\rangle = \frac{1}{\sqrt{3}} |F' = 3/2, M_{F'} = 1/2\rangle + \frac{\sqrt{2}}{3} |F' = 1/2, M_{F'} = 1/2\rangle.
\]
For further reference, we also write the wavefunction of the atoms excited from the $|F = 1/2, M_F = 1/2\rangle$ state:
\[
|\varphi\rangle = |F' = 3/2, M_{F'} = 3/2\rangle.
\]
Because the initial sublevels are incoherent, the wavefunctions $|\psi\rangle$ and $|\varphi\rangle$ are also mutually incoherent.
Expression (3.276) can be decomposed into the uncoupled basis $|M_{J'}, M_I\rangle$ using Clebsch-Gordan coefficients

$$|\psi\rangle = \left(\frac{1}{3} + \frac{2}{3}\right)|1, -1/2\rangle + \left(\sqrt{3} + \sqrt{3}\right)|0, 1/2\rangle$$

$$= |1, -1/2\rangle,$$ (3.278)

which shows explicitly that only the $M_{J'} = 1$ state for the electron is excited by the laser pulse, while the nucleus just “goes for the ride.”

A similar decomposition for the wavefunction (3.277) is trivial:

$$|\phi\rangle = |1, 1/2\rangle.$$ (3.279)

From Eqs. (3.278) and (3.279), we see that the nucleus, being in an incoherent mixture of the $M_I = \pm 1/2$ states with equal weight, remains unpolarized upon short-pulse excitation.

(c) In order to find the time dependence of nuclear polarization, we go back to Eq. (3.276), and add time dependence of the eigenfunctions by introducing the hyperfine frequency $\omega = (E_{F'=3/2} - E_{F'=1/2})/\hbar$ corresponding to the energy interval between the two hyperfine states:

$$|\psi(t)\rangle = \left[\frac{1}{\sqrt{3}} |F' = 3/2, M_{F'} = 1/2\rangle e^{-i\omega t} + \sqrt{2} |F' = 1/2, M_{F'} = 1/2\rangle e^{-i\omega t}\right] e^{-t/2\tau},$$ (3.280)

where $\tau$ is the lifetime of the $J' = 1$ state. Correspondingly, Eq. (3.278) becomes

$$|\psi(t)\rangle = \left[\left(\frac{1}{3} e^{-i\omega t} + \frac{2}{3}\right)|1, -1/2\rangle + \left(\sqrt{2} e^{-i\omega t} - \sqrt{2}\right)|0, 1/2\rangle \right] e^{-t/2\tau},$$ (3.281)

so that the average nuclear projection on the direction of the light circular polarization (taking into account also the atoms excited from the $M_{F'} = 1/2$ sublevel and assuming an initially equal distribution in the two ground state sublevels) for atoms in the excited state is:

$$\langle M_I \rangle \propto \left[\left|\frac{1}{3} e^{-i\omega t} + \frac{2}{3}\right|^2 \cdot \left(\frac{1}{2}\right) + \left|\sqrt{2} e^{-i\omega t} - \sqrt{2}\right|^2 \cdot \left(\frac{1}{2}\right) + \frac{1}{2}\right] e^{-t/\tau}$$

$$= \frac{4}{9} |1 - \cos \omega t| e^{-t/\tau}.$$ (3.282)

From this expression we see that nuclear polarization, while zero at $t = 0$, is generally non-zero at later times. The oscillations of the polarization (quantum beats) are superimposed on the exponential decay of the upper state.
THOMSON SCATTERING

(d) This discussion shows that an optical-pumping cycle consisting of a short-pulse excitation followed by spontaneous decay back to the ground state increases the population of the $M_F = M_I = 1/2$ state. Once there, the atoms (or, more precisely, their nuclei) are “trapped” as subsequent additional cycles cannot remove them from the $M_I = 1/2$ state. Of course, this conclusion is also true for continuous excitation, and this is, in fact, how $^{199}\text{Hg}$ nuclei are optically pumped in practice [see Happer (1972), for example]. Note that, while resolving hyperfine structure is not necessary for efficient pumping, it is necessary that the hyperfine frequency $\omega$ is not much smaller than the spontaneous relaxation rate $1/\tau$.

Note that, considering the results of Problem 3.19, even though we have accomplished optical pumping of the ground $J = 0$ state, as long as the upper-state hyperfine structure is unresolved, we can only probe total population of the ground state. In other words, we cannot optically detect that the ground state has been polarized.

3.21 Thomson scattering

Consider a free electron interacting with a light wave. Based on the classical model in which light scattering is due to the radiation of the accelerating electron, derive an expression for the total scattering cross-section. Neglect the recoil effects and the effects of the optical magnetic field. Formulate the conditions for such approximation to be valid.

Solution

The electric force on the electron is

$$
\vec{F} = -e\vec{E}\cos \omega t ,
$$

(3.283)

where $\vec{E}$ is the optical electric-field amplitude, $\omega$ is the frequency of the light, and we have chosen the phase of the wave arbitrarily. The electron accelerates upon the action of this force and so produces an oscillating dipole $\vec{d}$ with the second time derivative

$$
\ddot{\vec{d}} = \frac{e^2 \vec{E}}{m}\cos \omega t ,
$$

(3.284)

where $m$ is the electron mass. According to the classical dipole-radiation formulae, the total power radiated by the oscillating dipole is given by [Panofsky and Phillips...
which, upon the substitution of Eq. (3.284) and integration over one period of the light oscillation gives

\[ P = \frac{e^4 \varepsilon^2}{3m^2c^3} . \]  

(3.286)

By definition, the number of photons scattered per unit time by the electron is given by \( \Phi \sigma \), where \( \Phi \) is the incident photon flux, and \( \sigma \) is the sought-after scattering cross-section. In order to connect Eq. (3.286) with these quantities, we replace \( P \) with the number of photons scattered per unit time times the energy of a scattered photon, \( \hbar \omega \) (which is the same as that of an incident photon, as long as we neglect recoil). Also, the average incident light intensity, \( \Phi \hbar \omega \), is given by the average Poynting vector

\[ \Phi \hbar \omega = \frac{cE^2}{8\pi} . \]  

(3.287)

Solving Eq. (3.287) for \( E^2 \) and making the corresponding substitutions into Eq. (3.286), we see that the \( \hbar \) factor cancels (after all, our derivation is classical) along with \( \omega \), and we get

\[ \sigma = \frac{8\pi}{3} \left( \frac{e^2}{mc^2} \right)^2 = \frac{8\pi}{3} r_0^2 , \]  

(3.288)

where \( r_0 \approx 2.8 \cdot 10^{-13} \) cm is the classical radius of the electron.

In the derivation of Eq. (3.288) we have neglected photon recoil. A characteristic magnitude of the electron’s momentum change in a scattering process is

\[ \Delta p \sim \frac{\hbar \omega}{c} , \]  

(3.289)

which leads to a change in the electron’s kinetic energy of

\[ \Delta E = \frac{\Delta p^2}{2m} \sim \frac{\hbar^2 \omega^2}{mc^2} . \]  

(3.290)

As long as \( \hbar \omega \ll mc^2 \), the change of the electron’s energy, and, by energy conservation, the energy difference between the incident and the scattered photons, is \( \ll \hbar \omega \), which justifies the no recoil approximation.
In the derivation of Eq. (3.288) we also neglected the effect of the magnetic force on the electron. In other words, we assumed

$$\frac{ev}{c} B \ll e E .$$

Here $v$ is the amplitude of the electron’s velocity as it undergoes the light-induced oscillation, and $B = E$ is the amplitude of the light magnetic field. This condition is equivalent to saying that the electron’s motion is nonrelativistic, $v \ll c$, or, equivalently, that the electron’s displacement during half cycle of the oscillation is much smaller than the light wavelength. For visible light, achieving the relativistic regime requires power densities on the order of $10^{17}$ W/cm$^2$, a level readily achieved with modern ultra-short-pulse lasers. The relativistic regime signifies a host of interesting phenomena described by high-field electrodynamics (Hartemann, 2002), for example, generation of light at high harmonics of the input frequency in the course of the light interaction with the electron.

### 3.22 Classical model for a magnetic-dipole transition

When we discuss electric-dipole interactions of atoms with light, we often use the “electron-on-a-spring” model (see, for example, Problem 3.21).

![Electron density in pure hydrogen $1S$ and $2P$, $M = 1$ states. Shown are contour plots obtained using hydrogen radial wavefunctions and spherical harmonics. There is no net electric-dipole moment in either an $S$ or a $P$ state as the electron density is symmetric with respect to the nucleus.](image)

It is interesting to consider the correspondence between the classical “electron-on-a-spring” model and the quantum mechanical model of light-atom interactions (see Probs. 3.1, 3.3, and 3.4). Classically, in order to have electric-dipole radiation, we need an oscillating (or rotating) dipole. However, an atom in a particular energy eigenstate does not represent an oscillating dipole. An oscillating dipole requires a coherent superposition of non-degenerate states of opposite parity (one can see this, for example, by considering a superposition of an $s$- and a $p$-orbital, see...
Fig. 3.29 A superposition of the two states shown in Fig. 3.28 (of the form 
\( \left( |n = 1, L = 0, M = 0 \rangle + e^{-i\omega \tau_0} |n = 2, L = 1, M = 1 \rangle \right)/\sqrt{2} \) in the case shown here) corresponds to an electron displaced to one side of the nucleus. The electron density and the corresponding electric-dipole moment rotate around the nucleus at a frequency corresponding to the energy interval between the S and P states (one period of such a rotation is shown in the figure), leading to E1 radiation. The arrow indicates the magnitude and instantaneous direction of the electric dipole moment.

Figs. 3.28 and 3.29). Incidentally, these considerations show that there is no semi-classical picture for spontaneous emission from an excited state – semi-classically, such states are stationary.

Devise a similar model for magnetic-dipole (M1) interactions. It is helpful to begin by considering electron densities for states that are coupled in an M1 transition. For example, consider a transition between Zeeman components of an \( L = 1 \) state that are split in energy in a static magnetic field applied along \( z \). What does the superposition state look like in this situation? How does it evolve in time? Also discuss the correspondence of the classical and quantum pictures for magnetic-dipole radiation.

Solution

In order to visualize the mechanism of the magnetic-dipole radiation, as suggested, we turn to the simple case of an M1 transition between Zeeman components of an
**CLASSICAL MODEL FOR A MAGNETIC-DIPOLE TRANSITION**

**Fig. 3.30** Contour plots of the electron density in pure hydrogen $2P, M = 0$ and $2P, M = 1$ states.

**Fig. 3.31** Contour plots of the electron density for a coherent superposition $(|n = 2, L = 1, M = 0\rangle + \exp (-i\omega_{10}t)|n = 2, L = 1, M = 1\rangle)/\sqrt{2}$ at different times. The nonzero value of $\omega_{10}$ results from the Zeeman shift of the $M = 1$ sublevel in a static magnetic field. Shown is one period of Larmor precession. The arrow indicates the magnitude and instantaneous direction of the magnetic dipole moment.

$L = 1$ state that are split in energy in a static magnetic field applied along $z$. Let us look at the electron densities corresponding to various states (Figs. 3.30, 3.31). In this case, not only is there no electric dipole moment in the pure eigenstates, but neither is there any dipole moment in their coherent superpositions. A superposition corresponds to two electron-density “bulges” that are symmetric with respect to the nucleus, but are displaced in the opposite directions with respect to the $x$-$y$
In the presence of a \( z \)-directed magnetic field, these bulges rotate around the \( z \)-axis at the Larmor frequency. It is easy to see from the definition of the magnetic dipole moment (see Problem 1.15)

\[
\vec{m} = \frac{1}{2c} \int \vec{r} \times \vec{j}(\vec{r}) \, d^3r
\]

(3.291)

(here \( \vec{j} \) is the electric-current density) that the instantaneous direction of the system’s magnetic dipole moment is tilted with respect to the \( z \)-axis, and is rotating around this axis at the Larmor frequency, causing M1 radiation.

Note that a single rotating bulge symmetric with respect to the \( x-y \) plane would be a poor model in this case. First, such a distribution has an electric dipole moment. Second, although such a system has a magnetic-dipole moment, it does not change with time, and thus does not produce M1 radiation.

### 3.23 Nonlinear three-wave mixing in isotropic chiral media

Usually, second-order nonlinear susceptibility, \( \chi^{(2)} \), is zero for an isotropic medium because most common isotropic media are centrosymmetric, i.e., their properties are invariant under spatial inversion [see, for example, Boyd (2003)]. However, as the following example shows, just because a medium is isotropic it does not necessarily follow that it is centrosymmetric!

Consider a gas or a liquid solution of chiral molecules. Such a medium is optically active – it rotates the plane of polarization of linearly polarized light propagating through the medium. The fact that the medium is isotropic means that the rotation angle does not depend either on the direction of light propagation or on the direction of the linear polarization.

On the basis of symmetry considerations, argue that:

(a) the second-order susceptibility \( \chi^{(2)} \) is generally non-zero in such a medium (in the course of this argument recall why \( \chi^{(2)} = 0 \) for isotropic centrosymmetric media);

(b) sum- and difference-frequency generation are forbidden in a geometry where all three light beams (the two input beams and the beam generated as a result of the nonlinear mixing) are collinear;

and

\[18\] The bulges occur in the regions of space where the \( M = 0 \) and the \( M = 1 \) parts of the wavefunction interfere constructively, i.e., where these two parts are in phase. Conversely, the electron density is low where these two parts are out of phase and interfere destructively. The relative phases of the two components can be easily deduced by examining the explicit form of the spherical harmonics \( Y^M_L(\theta, \phi) \).
(c) second-harmonic generation is forbidden.

(d) Electro-optical rotation can be thought of in terms of a $\chi^{(2)}$ wave-mixing process, where one of the “waves” is the dc field. Suppose a static electric field is applied along the direction of propagation of linearly polarized light in an isotropic chiral medium. Can there be optical rotation linear in the applied static field?

**Solution**

(a) Suppose two electromagnetic waves with electric-field amplitudes $\vec{E}^1$ and $\vec{E}^2$ are present in the medium. In general, second-order nonlinear-optical processes (a.k.a. three-wave mixing) arise due to the medium’s polarization which is bi-linear in these amplitudes:

$$\mathcal{P}^{(2)}_i \propto \chi^{(2)}_{ijk} E^1_j E^2_k,$$

where $\chi^{(2)}_{ijk}$ is the second-order nonlinear susceptibility tensor.

For an isotropic medium, any quantity describing the medium, including $\chi^{(2)}_{ijk}$, should be invariant with respect to rotations of the coordinate frame. This does not leave us much choice for constructing the susceptibility tensor, in fact, there is only one possibility available [see, for example, Riley *et al.* (2002), Sec. 21.8-9, or Weisstein (2005)]:

$$\chi^{(2)}_{ijk} \propto \epsilon_{ijk},$$

where $\epsilon_{ijk}$ is the completely antisymmetric (Levi-Civita) tensor.

Thus, we have:

$$\mathcal{P}^{(2)}_i = c\epsilon_{ijk} E^1_j E^2_k,$$

where $c$ is the proportionality constant. Alternatively, this can be written as

$$\vec{\mathcal{P}}^{(2)} = c\vec{E}^1 \times \vec{E}^2.$$

For a “normal” centrosymmetric medium, the proportionality coefficient $c$ is just a scalar because all properties of the medium must remain invariant under spatial inversion. Let us examine what happens to the left-hand and right-hand side of Eq. (3.295) upon spatial inversion. Polarization of the medium $\vec{\mathcal{P}}^{(2)}$ is a polar vector, and thus changes sign upon spatial inversion. On the right-hand side, however, we have a product of two polar electric-field vectors, which is an axial vector invariant with respect to spatial inversion. This can only be the case when $c$ (and, correspondingly, $\vec{\mathcal{P}}^{(2)}$) is equal to zero. This proves the well-known fact that
three-wave mixing is forbidden in isotropic media which are invariant with respect to spatial inversion.

A chiral medium, however, is not invariant with respect to inversion because this operation converts left-handed molecules into right-handed ones and vice versa. Therefore, there is a possibility that a part of the proportionality coefficient \( c \) is actually a pseudoscalar, i.e., a rotationally-invariant scalar quantity that flips sign upon spatial inversion. With this, both sides of Eq. (3.295) are odd with respect to spatial inversion, and the second-order nonlinear polarization is generally non-zero.

(b) Nevertheless, the specific form of Eq. (3.295) restricts the allowed types of three-wave mixing. For example, the nonlinear polarization is zero for input waves of the same polarization. Also, if the two waves are co-propagating, the induced polarization is along the propagation direction, so the resultant wave generated by this polarization cannot propagate in the same direction (which would violate transversality – the fact that in isotropic, non-dissipative media the electric and magnetic fields of light must be orthogonal to the direction of light propagation).

(c) Suppose now that the two input waves are of the same frequency. At each point in the medium, we have two fields applied, however, according to the superposition principle, we can take a vector sum of these fields to obtain just one resultant field (with a generally complex polarization). But the vector product of any vector with itself is zero, and Eq. (3.295) once again leads us to the conclusion that three-wave mixing is forbidden in this case, i.e., coherent second-harmonic generation does not occur in isotropic chiral media.\(^{19}\)

(d) Let us now consider the possibility of electro-optical rotation. The geometry of the problem is such that if we have initial light-field polarization \( \vec{\varepsilon}_0 \), and a static field \( \vec{E}_{dc} \), then the light polarization \( \vec{\varepsilon}' \) upon propagation through a thin slice of the medium can be written as

\[
\vec{\varepsilon}' = \vec{\varepsilon}_0 + a \vec{E}_{dc} \times \vec{\varepsilon}_0 .
\]  

\(^{19}\) Here we have shown that two input waves of the same frequency cannot produce coherent second-harmonic output (independently of the waves' polarizations or propagation directions) in isotropic media in the framework of the dipole approximation. It turns out that, in the case of a single input beam, the result holds true even if all possible higher multipoles are considered (Andrews and Blake 1988). We can give a simple proof of this [different from the one by Andrews and Blake (1988)], once again, based on symmetry arguments. In this geometry, the only independent vectors in the problem are the amplitude \( \vec{E}_{1H} \) of the wave at the fundamental frequency, its wave vector \( \vec{k} \), and the polarization of the second-harmonic wave \( \vec{E}_{2H} \) (the second-harmonic wave would need to have the wave vector \( 2\vec{k} \)). Out of these vectors, it is impossible to construct an expression for the amplitude of the process that would be quadratic in \( \vec{E}_{1H} \), linear in \( \vec{E}_{2H} \), and would not violate transversality, i.e., the requirement that \( \vec{E}_{1H} \cdot \vec{k} = \vec{E}_{2H} \cdot \vec{k} = 0 \).
Here \( a \) is a pseudoscalar proportional to the pseudoscalar part of \( c \). Equation (3.296) can also be rewritten as

\[
\vec{\varepsilon}' \times \vec{\varepsilon}_0 = -a \vec{E}_{dc}.
\]

Equation (3.297) passes the test of spatial-inversion invariance; however, it fails the test of time-reversal invariance. Indeed, if we reverse the direction of time (which, in this case, would be equivalent to sending the light beam backwards), we would need to interchange the initial and final polarization vectors, which would flip the sign on the left-hand side of Eq. (3.297), while the right-hand side of Eq. (3.297) remains unchanged. We thus see that nonlinear electro-optical activity is forbidden. More generally, we see that three-wave mixing in isotropic chiral media can only occur between non-collinear waves of three different frequencies.

The fact that coherent wave-mixing, for example, second-harmonic generation is forbidden does not actually mean that if one shines light at fundamental frequency onto a sample there will be no second-harmonic light whatsoever coming out of the sample. Imagine a container with a large number of second-harmonic-generation crystals that are randomly oriented. The medium is macroscopically isotropic, but locally, it is highly anisotropic, so second-harmonic generation can occur on an individual crystal. The overall output will depend on imperfect cancellation of the amplitudes generated in different crystals, and will scale linearly with the number of crystals (as opposed to coherent second-harmonic generation where the output power scales as the square of the participating dipoles or the length of the medium). An experimental study of second-harmonic generation in microscopically isotropic water suspensions of anisotropic biological “particles” and the associated theory have been discussed by Allcock et al. (1996).

In this problem, we have considered various cases where coherent \( \chi^{(2)} \) processes are forbidden in the bulk. In most cases, however, these prohibitions fail at the interfaces between different media where the media are no longer isotropic. This is the basis for powerful non-linear optical techniques to study surfaces and interfaces [see, for example, Shen (1989)].

### 3.24 A negatively refracting atomic vapor?

Left-handed materials are media where the electric permittivity \( \varepsilon \) and the magnetic permeability \( \mu \) are both negative (the term is unfortunate and potentially confusing since “left-handedness” in this context is different from chirality normally associated with handedness!). It can be shown from Maxwell’s equations [see, for example, Veselago (2003), Pendry and Smith (2004), and Milonni (2004)] that, in this case, the refractive index is also negative, i.e., \( n = -\sqrt{\varepsilon \mu} \). For an electromagnetic wave propagating in such a medium, the wave vector (\( \vec{k} \)) is in the direction...
opposite to $\vec{E} \times \vec{H}$, so, for example, one needs to use the left-hand instead of the right-hand rule to find the direction of $\vec{H}$ from the directions of $\vec{k}$ and $\vec{E}$.

Such materials are of particular interest since a “perfect” lens [Pendry (2000)], not subject to the ordinary diffraction limit, can be made with a material having an index of refraction equal to $-1$ [the concept of a perfect lens and other fascinating properties of electromagnetic wave propagation through negatively refracting materials are reviewed, for example, by Veselago (2003) and Pendry (2004a); see also Smith (2005) and Milonni (2004)].

Most materials with negative refractive indices work only for electromagnetic radiation in the radio-frequency and microwave domains. These so-called meta-materials are artificial structures built out of discrete elements such as split metal rings, wires, etc. However, it should be noted that recently Zhang et al. (2005) produced a metal-dielectric-metal multilayer material that exhibited a negative index of refraction for infrared light with wavelength around 2 $\mu$m. The production of this metamaterial operating in the near-IR required sophisticated nanofabrication techniques to create the required nanometer-scale spatially periodic structure.

Is it possible that under certain conditions an atomic vapor could act as a negatively refracting material? First see what one would want in terms of the energy levels and transitions in the atom. Next, consider if such a system can be found in practice. Estimate the required density of the atoms. (Make sure the system is reasonably transparent!)

Solution

One idea for making a negatively refracting atomic vapor could be to exploit the fact that, for light frequencies above an atomic resonance, the permittivity of the vapor drops below unity. For a sufficiently dense vapor, it may become negative. In order to create the desired material, we would need both the electric permittivity and magnetic permeability to be simultaneously negative.

We begin with the discussion of the electric permittivity and limit ourselves to the electron-on-a-spring model of an atom (since there is only a single resonance frequency for such a system, this is, in other words, a two-level atom). In this model, the electric susceptibility as a function of frequency $\omega$ is found to be [see, for example, Griffiths (1999), Section 9.4.3]:

$$
\varepsilon = 1 + \frac{4\pi N e^2}{m_e} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma \omega}.
$$

(3.298)

Here $N$ is the atomic number density, and $\omega_0$ and $\gamma$ are the resonance frequency and width, respectively. If we denote the detuning from resonance $\omega - \omega_0 = \Delta$,
we can re-write Eq. (3.298) as
\[ \varepsilon = 1 - \frac{4\pi Ne^2}{m_e} \cdot \frac{(\omega_0 + \omega)\Delta - i\gamma\omega}{(\omega_0 + \omega)^2 + \gamma^2\omega^2}. \] (3.299)

Note that the real part of the index of refraction is proportional to \( \Delta \) far from resonance whereas the imaginary part decreases as \( \Delta^2 \).

In order for the permittivity \( \varepsilon \) to be essentially real, the frequency \( \omega \) has to be sufficiently far away from resonance where we can neglect the imaginary term, in other words, \( \Delta \gg \gamma \), so that
\[ \varepsilon \approx 1 - \frac{4\pi Ne^2}{m_e} \cdot \frac{1}{(\omega_0 + \omega)\Delta}. \] (3.300)

In order for the permittivity to be negative, we need to have \( \omega > \omega_0 \) (i.e., \( \Delta > 0 \)), and
\[ N > \frac{m_e(\omega_0 + \omega)\Delta}{4\pi e^2}. \] (3.301)

From Eq. (3.301), it is seen that for large \( \Delta \), the condition on the density can be re-written as
\[ N \gtrsim \frac{m_e^2 \omega_0^2}{e^2} \approx \frac{m_e^2 (m_e e^4 / \hbar^2)^2}{\hbar^2 e^2} = \left( \frac{m_e e^2}{\hbar^2} \right)^3 \sim \frac{1}{a_0^3}, \] (3.302)
i.e., the density should be greater than the density of condensed matter, about \( 10^{24} \) atoms/cm\(^3\), which would mean that the system was no longer a vapor.\(^{20}\)

Here we have used the fact that the energy difference between the atomic states \( \hbar\omega_0 \) should be on the order of the Bohr energy \( e^2 / a_0 \) (see Appendix A).

On the other hand, the density requirement [Eq. (3.301)] is significantly relaxed as the frequency \( \omega \) approaches the resonance frequency \( \omega_0 \). From Eqs. (3.301) and (3.302), we find that closer to resonance we require
\[ N \gtrsim \frac{1}{a_0^3 \omega_0}. \] (3.303)

Recall that for the refractive index to remain real we cannot operate too close to resonance, so there is a lower limit on \( \Delta \) of several times the resonance width \( \gamma \).

At the densities \( N \) necessary to satisfy Eq. (3.303), \( \gamma \) is dominated by pressure broadening, i.e.,
\[ \gamma \sim N\sigma_p v, \] (3.304)
where \( \sigma_p \) is the pressure broadening cross-section and \( v \) is the thermal velocity of the atoms (for a typical room-temperature gas, pressure broadening dominates

\(^{20}\) Incidentally, there do exist solids with negative electric permittivity. In addition, dense plasmas have been also produced that have \( \varepsilon < 0 \).
when $N\sigma_pv \gtrsim 2\pi \times 1$ GHz, where 1 GHz is the typical value of the Doppler width for an optical transition). Re-writing the requirement (3.303) by setting $\Delta \sim \gamma$ and using the expression (3.304) for $\gamma$, we discover that the condition becomes independent of $N$:

$$1 \gtrsim \frac{1}{a_0^3} \frac{\sigma_pv}{\omega_0}.$$  \hspace{1cm} (3.305)

The question now becomes whether or not the inequality (3.305) can be satisfied by typical atoms. Atomic pressure broadening cross-sections are usually in the range of $10^{-15} - 10^{-14}$ cm$^2$ (see Appendix A), so in fact it is possible for a room temperature gas (where $v \sim 10^4$ cm/s) to achieve negative permittivities near resonance. For these conditions, the atomic density will be $N \sim 10^{18}$ cm$^{-3}$, six orders of magnitude smaller than in the far-detuned case, and $\varepsilon$ reaches negative values of order unity. Note, as Eq. (3.305) implies, that increasing the density past this point does not improve the situation. However, note that the condition (3.305) does depend on the atoms’ velocity $v$, so by using laser cooling (where thermal velocities can reach $\lesssim 1$ cm/s) or cryogenic techniques, the required density to achieve negative permittivities can be further reduced.

With the realization of the difficulties that arise when one is attempting to achieve an atomic vapor with negative electric permittivity, we now turn to the discussion of the magnetic permeability. Again, we will use a two-level model; however, in this case, the levels must be coupled by magnetic-dipole, rather than electric-dipole interaction. We can obtain the expression for the magnetic permittivity by analogy with Eq. (3.298) if we first rewrite it to introduce the transition dipole moment $d$ as

$$\varepsilon = 1 + \frac{4\pi N d^2}{m_e a_0^2} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}.$$ \hspace{1cm} (3.306)

Then, it is clear that the permeability is of the form

$$\mu = 1 + \frac{4\pi N \mu_0^2}{m_e a_0^2} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma' \omega},$$ \hspace{1cm} (3.307)

where $\mu_0$ is the Bohr magneton, $\omega'$ and $\gamma'$ are the frequency and width of the corresponding magnetic-dipole transition.$^{21}$

We can now easily obtain the conditions on the density necessary to make the permeability negative by following the same line of reasoning employed for the electric permittivity. The required density is thus the same as for the case of the

$^{21}$ Here, we treat $\mu$ on the same footing as $\varepsilon$. Some authors [e.g., Landau and Lifshitz (1995), Section 103] prefer, instead of treating electric and magnetic effects symmetrically, to take advantage of the relation between the electric and magnetic fields in an electromagnetic wave and introduce the magnetic effects via spatial dispersion of $\varepsilon$, i.e., the dependence of $\varepsilon$ on the wave vector.
electric permittivity, except increased by a factor of \((d/\mu_0)^2 \sim 10^5\). In the far-detuned regime, this would require densities larger than those of typical condensed matter, ruling out this possibility, while in the regime where \(\omega \rightarrow \omega_0\), typical levels of pressure broadening would prohibit negative values for \(\mu\) for room temperature gases. For ultracold atomic gases, the required density \((N \sim 10^{19} \text{ cm}^{-3})\) is far too large for present technology.

Not only are the conditions for negative permittivity and negative permeability extraordinarily difficult to achieve in an atomic vapor, the conditions must be simultaneously satisfied at a particular frequency. We are thus left with a pessimistic assessment of the prospects of “left-handed” atomic vapors.

In our above considerations we have assumed that the electric dipole (E1) and magnetic dipole (M1) transitions are between the ground state of the atom and two distinct upper states, so the permittivity and permeability can be calculated independently. This seems a reasonable assumption, since E1 transitions occur between states of opposite parity and M1 transitions occur between states of the same parity. Recently, there has been a suggestion by Pendry (2004b) that the above requirements can be loosened somewhat in a chiral medium (molecular vapors, for example). The idea is similar to that employed in, for example, atomic parity violation experiments that take advantage of Stark-induced transitions (see discussion in Problem 4.5). In a chiral medium, the states have mixed parity, and thus transitions have both E1 amplitudes (proportional to \(d\)) and M1 amplitudes (proportional to \(\mu\)). Interference between the M1 and E1 amplitudes enhances the magnetic dipole transition, and therefore the required density for negative permeability in a chiral medium is only a factor of \(\sim d/\mu_0 \sim 2 \times 137\) larger than that for the permittivity. It is interesting to note that a similar situation can arise when nearly degenerate opposite parity levels are mixed with external fields, as in the case of hydrogen and dysprosium [Budker et al. (1994)]. Even so, achieving the vapor density \((\sim 10^{20} \text{ atoms/cm}^3)\) required for negative permeability in the small detuning regime would necessitate anomalously small pressure broadening. Using cold chiral molecules can reduce the required vapor density, but remains at present a technically difficult path to achieving a negatively refracting vapor.

One might wonder if electromagnetically induced transparency (EIT) in a multi-level atomic system might offer a possible solution to this dilemma — permitting high densities while maintaining narrow linewidths and small absorption. Yet it appears that even with EIT the stringent requirements on the magnetic permeability will be difficult to achieve in atomic vapors [Oktel and Mustecaplioglu (2004)]. The use of quantum interference effects similar to EIT are being explored as a way to generate chirality while minimizing absorption [see, for example, Kästel et al. (2007)].
3.25  Light propagation in anisotropic crystals

Recall the following results pertaining to linear plane-wave-light propagation in a transparent non-gyrotropic, anisotropic medium such as a uniaxial or biaxial crystal, for which the dielectric tensor $\varepsilon_{ij}$ is real and symmetric [these properties follow from energy conservation: see, for example, Fowles (1975), Section 6.7; Landau et al (1995), Section 97; Born and Wolf (1980), Chap. 14]:

- For a given direction of the wave vector, there are two polarization eigen-modes, where the polarization is characterized by the direction of the electric displacement vector $\vec{D}$. An eigenmode is a wave that propagates in the crystal maintaining its polarization.
- The two eigenmodes are linearly polarized with mutually orthogonal directions of $\vec{D}$.

Now on to the questions:

(a) Why are the eigenmodes characterized by $\vec{D}$ rather than the electric field $\vec{E}$?

(b) Why are there two eigenmodes?

(c) Why do the two eigenmodes correspond to mutually orthogonal directions of $\vec{D}$?

(d) Why are the eigenmodes linearly polarized?

(e) Comment on the analogies between this problem and quantum mechanics.

Solution

(a) For the case of a monochromatic light wave (of frequency $\omega$, so all quantities have temporal dependence $e^{-i\omega t}$), Maxwell’s equations take on the form:

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{H}}{\partial t} = \frac{i\omega}{c} \vec{H}, \quad (3.308)$$

$$\vec{\nabla} \times \vec{H} = \frac{1}{c} \frac{\partial \vec{D}}{\partial t} = -\frac{i\omega}{c} \vec{D}. \quad (3.309)$$
Substituting the spatial dependence of all quantities in the form of $e^{i\vec{k}\cdot\vec{r}}$ (where $\vec{k}$ is the wave vector), we find:

$$\vec{k} \times \vec{E} = \frac{\omega}{c} \vec{H}, \quad (3.310)$$

$$\vec{k} \times \vec{H} = -\frac{\omega}{c} \vec{D}. \quad (3.311)$$

Equation (3.310) indicates that $\vec{k}$ is perpendicular to $\vec{H}$. Also, Eq. (3.311) shows that $\vec{D}$ is perpendicular to both $\vec{k}$ and $\vec{H}$. Thus, the vectors $\vec{k}$, $\vec{D}$, and $\vec{H}$ are all mutually perpendicular. On the other hand, while $\vec{E}$ is perpendicular to $\vec{H}$ [Eq. (3.310)], it is not, in general, perpendicular to $\vec{k}$ in an anisotropic medium (Fig. 3.32).

![Fig. 3.32](image)

**FIG. 3.32** Various vectors describing plane-wave propagation in an anisotropic medium.

(b-d) [Here we follow Bredov, et al. (1985), Section 29.]

First, let us eliminate $\vec{H}$ from Eqs. (3.310) and (3.311) to obtain the wave equation

$$\vec{k} \times \vec{k} \times \vec{E} = -\frac{\omega^2}{c^2} \vec{D}, \quad (3.312)$$

which, using the “BAC-minus-CAB” vector identity, becomes

$$\vec{k}(\vec{k} \cdot \vec{E}) - \vec{E}k^2 = -\frac{\omega^2}{c^2} \vec{D}. \quad (3.313)$$
This is a vector equation. We will choose a coordinate system with one of the axes along $\vec{k}$, and look at the projections of each of the terms onto an axis ($\alpha$) orthogonal to $\vec{k}$. Since $\vec{k}$ has zero projection on this axis, the first term in Eq. (3.313) does not contribute, and we have:

$$\mathcal{E}_\alpha k^2 = \frac{\omega^2}{c^2} D_\alpha .$$  \hspace{1cm} (3.314)

Until this point, we have only used Maxwell’s equations, and have not used any information about the properties of the medium. All the relevant properties are contained in the material equations

$$D_i = \varepsilon_{ij} E_j .$$  \hspace{1cm} (3.315)

These relations can be inverted to read

$$E_i = \varepsilon^{-1}_{ij} D_j .$$  \hspace{1cm} (3.316)

Since $\varepsilon_{ij}$ is symmetric, so is its inverse, the inverse permittivity tensor $\varepsilon^{-1}_{ij}$ [see, for example, Riley et al. (2002), Section 8.12].

Substituting Eq. (3.316) into Eq. (3.314), we have

$$\varepsilon^{-1}_{\alpha\beta} D_\beta k^2 = \frac{\omega^2}{c^2} D_\alpha .$$  \hspace{1cm} (3.317)

In this equation, since $\vec{D}$ is confined to a plane, there are only two possible values of the indices $\alpha$ and $\beta$, and the relevant components of $\varepsilon^{-1}_{\alpha\beta}$ correspond to a $2 \times 2$ symmetric matrix.

Equation (3.317) can be regarded as an eigenvalue problem for the the $2 \times 2$ tensor $\varepsilon^{-1}$, where the eigenvalues are $n^{-2} = \omega^2/(k^2c^2)$, and $n$ is the effective refractive index for a given eigenmode. We now recall that any symmetric tensor can be diagonalized, and the principal axes are orthogonal to each other [see, for example, Riley et al. (2002), Section 8.13]. Thus, the eigenpolarizations correspond to two orthogonal directions of $\vec{D}$ along these principal axes, so the two eigenpolarizations are linear.

(e) The analogy with quantum mechanics can be made rather complete. In quantum mechanics, we often talk about temporal evolution of the wavefunction governed by the Hamiltonian. In this case, we deal with spatial propagation of an electromagnetic wave, and we were able to reduce the propagation problem, using the Maxwell’s equations and the material relations, to the eigenvalue problem (3.317) analogous to that of finding eigenstates in a quantum-mechanical two-level system. It is interesting to note that “orthogonality” of eigenstates corresponding to distinct eigenvalues, which in quantum mechanics usually refers to Hilbert space, here can be understood literally – the two eigenpolarizations are orthogonal in real space.
3.26 Electromagnetically induced transparency (EIT)

The basic phenomenon of electromagnetically induced transparency involves three levels and two light fields [Fig. 3.33(a)]. Suppose that, in the absence of light, all atoms reside in state $|A\rangle$. If a weak field (the probe field) is applied on resonance with the $|A\rangle \rightarrow |C\rangle$ transition, in the absence of other light fields, the probe field experiences absorption. However, if a strong light field (the drive field) is applied on resonance with the adjacent transition between levels $|B\rangle$ and $|C\rangle$, absorption on the probe transition vanishes. [There is vast literature available on the subject of EIT. A few accessible references include papers by Vrijen et al. (1996), Harris (1997), and Kasapi (1996).]

\textbf{Fig. 3.33} (a) Illustration of the basic phenomenon of electromagnetically induced transparency (EIT). Absorption on the probe ($|A\rangle \rightarrow |C\rangle$) transition is suppressed when a strong drive field is applied on the adjacent transition between levels $|B\rangle$ and $|C\rangle$. (b) EIT in the case where light frequencies are detuned from their respective one-photon resonances.

(a) Give a simple quantum-mechanical explanation of the EIT phenomenon. In particular, show that there is a coherent superposition of states $|A\rangle$ and $|B\rangle$ that does not absorb light from either probe or drive field (a dark state). Make the simplifying assumption that both light fields are monochromatic.

(b) What role does spontaneous emission play in EIT? For example, is spontaneous emission necessary to put atoms originally prepared in state $|A\rangle$ into the dark coherent superposition of states $|A\rangle$ and $|B\rangle$?

(c) In part (a), we considered the case where both the probe and the drive fields are tuned to their respective one-photon resonances. In this case, the two-photon (Raman) resonance condition is

$$h(\omega_p - \omega_d) = E_B - E_A ,$$

(3.318)
where \( \omega_p \) and \( \omega_d \) are the probe and drive frequencies, respectively, and \( E_A, E_B \) are the energies of the corresponding states.

Now consider the same system, except that the light fields are not exactly on resonance with the corresponding one-photon transitions [Fig. 3.33(b)]. Since the strong drive light field is off-resonant, it causes ac-Stark shifts of the levels \( |B\rangle \) and \( |C\rangle \) (see Problem 2.7), so the two-photon (Raman) resonance condition is no longer given by Eq. (3.318).

In this case, at what frequency of the probe light does absorption vanish due to EIT?

**Solution**

(a) The basic EIT phenomenon can be understood by considering the interaction of an atomic system with the bichromatic light field consisting of the probe and drive light fields. The states \( |A\rangle \) and \( |B\rangle \) are both coupled to the upper state \( |C\rangle \) by the light field. In general, we can consider the interaction with \( |C\rangle \) of any *coherent superposition* of states \( |A\rangle \) and \( |B\rangle \):

\[
|\psi\rangle = a|A\rangle + b|B\rangle , \tag{3.319}
\]

where \( a \) and \( b \) are some constant complex coefficients.

The amplitude \( A \) for photon absorption in the dipole approximation is proportional to the product of the dipole transition matrix element and the optical electric field \( \vec{d} \cdot \vec{E} \) (see, for example, Problem 3.4). In the present case,

\[
A \propto \langle C|\vec{d} \cdot \vec{E}|\psi\rangle = a\langle C|d|A\rangle E_p + b\langle C|d|B\rangle E_d = ad_{CA}E_p + bd_{CB}E_d , \tag{3.320}
\]

where \( E_p \) is the amplitude of the probe field and \( E_d \) is the amplitude of the drive field. In the above we neglect far off-resonant interactions such as the direct interaction of the drive light field with the \( |A\rangle \rightarrow |C\rangle \) transition.

Here an essential point is that we add transition amplitudes (not probabilities). The amplitude \( A \) in Eq. (3.320) vanishes when

\[
b = -\frac{d_{CA}E_p}{d_{CB}E_d}a . \tag{3.321}
\]

When the condition (3.321) is satisfied, the atoms are in a *dark state*, \( |\psi_{\text{dark}}\rangle \), where they do not interact with light (see also Problems 3.9 and 3.10). Note that choosing the ratio of the drive and probe intensities sufficiently high, we can have essentially all of the atomic population remaining in state \( |A\rangle \).

Let us recap the situation. The atoms are in state \( |A\rangle \), the probe light is applied on resonance with the \( |A\rangle \rightarrow |C\rangle \) transition, but there is no absorption, where there would have been absorption in the absence of the light driving the \( |B\rangle \leftrightarrow |C\rangle \) transition. This is EIT.
But how does the atomic system end up in the dark state? It turns out that in practice preparing the system in the dark state is not difficult, since the system tends to self-adjust to be in the appropriate state for EIT to occur. The creation of a dark coherent superposition of atomic states is also known as coherent population trapping (see Problem 3.10). We briefly discuss this in the solution to part (b). Coherent population trapping is reviewed by Arimondo (1996) and coherent population transfer is reviewed by Bergmann et al. (1998).

(b) This is indeed a somewhat tricky question. Clearly there must be spontaneous emission in the system: we have level $|C\rangle$ that lies above levels $|A\rangle$ and $|B\rangle$ and has non-zero electric-dipole matrix elements coupling to both $|A\rangle$ and $|B\rangle$. Thus, if we populate level $|C\rangle$, there is necessarily spontaneous emission to the lower levels.

While this is true, it does not answer the question of the role of spontaneous emission in the generation of EIT.

It turns out that in some instances, spontaneous emission does indeed play a role in the creation of EIT. Imagine a situation where all atoms are initially in state $|A\rangle$, and the light fields are turned on abruptly. State $|A\rangle$ is a superposition of the dark state and the bright state (where the bright state is the coherent superposition of states $|A\rangle$ and $|B\rangle$ orthogonal to $|\psi_{\text{dark}}\rangle$). The dark state component of $|A\rangle$ does not interact with light, but the bright component does. Therefore, after the light is turned on, some atoms will be excited. Following the excitation, an atom can spontaneously decay to levels $|A\rangle$ and $|B\rangle$, which may land it either in the bright or the dark state. Since atoms are not re-excited from the dark state, eventually, all atoms are pumped into $|\psi_{\text{dark}}\rangle$.

This scenario, however, does not mean that spontaneous emission is always necessary for establishing EIT. It turns out that it is possible to put the system into the dark state without having any spontaneous emission to the lower levels. Here is how it can be done. Let us first turn on the drive field alone. This light drives transitions between two empty levels ($|B\rangle$ and $|C\rangle$) and there is no fluorescence. This means that the system happens to already be in the dark state [$|\psi_{\text{dark}}\rangle = |A\rangle$ for this particular light field, $E_p = 0$, see Eq. (3.321)]. Now we have to exercise some caution in turning on the probe field – if we turn it on abruptly, there will be fluorescence. However, if we turn this field on adiabatically (see Problems 2.6 and 3.17), the system will remain in the dark state. The atoms evolve into a superposition of the states $|A\rangle$ and $|B\rangle$, and no spontaneous decay ever occurs!

This situation is directly analogous to many different adiabatic following problems, for example, a classic problem in polarization optics where the goal is to rotate the direction of linear polarization of a light beam if only (ideal) dichroic polarizers are available. The trick is to pass the light through a sequence of such polarizers, each rotated by a very small angle with respect to its input linear polarization. In such an arrangement, the polarization rotation angle per polarizer is
φ/N, where φ is the total desired rotation angle, N is the number of polarizers. The fractional light-power loss per polarizer is \( \frac{1}{2} (\phi/N)^2 \) (for sufficiently large N). Thus, the total loss (analogous to fluorescence in our problem) is \( \phi^2/(2N) \) and can be made as small as desired by increasing N.

The method of coherent population transfer of population between levels discussed in this part is known as Stimulated Raman Adiabatic Passage (STIRAP) [see Bergmann et al. (1998) and also the discussion of adiabatic passage in Problem 2.6].

(c) The dark state in our three-level system is decoupled from the light and thus is not subject to light shifts. Therefore EIT occurs when the condition (3.318) is satisfied, while the two-photon (Raman) resonance occurs at an ac-Stark shifted frequency.

Reality check: It often happens that various nonlinear optical processes occur concurrently, and it is not so easy to disentangle them and apply the simplified reasoning we have been practicing above in a realistic situation.

Let us illustrate this by checking our understanding of EIT against the results of a full quantum-mechanical calculation for the three-level system interacting with two light fields (as in Fig. 3.33). The calculation is set up in the following way. Atoms are assumed to leave at a rate γ the region where they interact with the bichromatic light field (independently of which atomic state they are in). The depletion of the total population is compensated by assuming the same number of atoms entering the interaction region. The entering atoms are in the ground state \( |A\rangle \). Figure 3.34 shows the transmission coefficient (as a function of the probe frequency, in relative units) of the probe light going through a thin atomic sample for various conditions:

(a) no drive field,
(b) drive field resonant with the \( |B\rangle \leftrightarrow |C\rangle \) transition, and
(c) drive field detuned by one natural width \( \gamma_0 \) of level \( |C\rangle \) towards lower frequencies.

It is also instructive to look at the steady-state populations of each of the states as a function of the probe frequency tuning (Fig. 3.35). Here state \( |C\rangle \) is assumed to spontaneously decay to states \( |A\rangle \) and \( |B\rangle \) with branching ratios 1/2 for each of the two decay channels. The latter plot can also be compared with the case of an open system where state \( |C\rangle \) spontaneously decays predominantly to states other than \( |A\rangle \) and \( |B\rangle \) (Fig. 3.36). In the latter case, for a weak probe field, the absorption spectrum is exactly the same as that shown in Fig. 3.34, while the populations of states \( |B\rangle \) and \( |C\rangle \) are obviously very different.

We leave it to the reader to identify and discuss various features of the transmission and population distribution profiles shown in Figs. 3.34, 3.35 and 3.36.
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Fig. 3.34 (a) Transmission of probe light in the absence of the drive field as a function of the probe frequency detuning $\Delta_p$ from the $|A\rangle \rightarrow |C\rangle$ resonance expressed in the units of the natural width of level $|C\rangle$, $\gamma_0$. Levels $|A\rangle$ and $|B\rangle$ do not decay, but atoms leave the interaction region (and are replenished) at a rate of $\gamma = 0.05\gamma_0$. (b) Same as (a) but in the presence of the drive field, with the drive frequency tuned to the $|B\rangle \leftrightarrow |C\rangle$ resonance (drive detuning represented by solid vertical line). The resonant Rabi frequency for the drive field is $0.8\gamma_0$. Dashed line indicates probe absorption without drive field. (c) Same as (b) but with the drive frequency tuned by $\gamma_0$ towards lower frequencies from the $|B\rangle \leftrightarrow |C\rangle$ resonance. Figure courtesy S. M. Rochester.

This is a common research task for both experimentalists and theorists: applying physical models to understand graphical representations of data or calculations. A detailed look at a closely related problem where analogous behavior is observed, namely a closed three-level system where atoms do not enter or leave the interaction region, including an analytic calculation of the lineshapes, is given by Lounis and Cohen-Tannoudji (1992).
Fig. 3.35 Steady-state populations of levels $|A\rangle$, $|B\rangle$, and $|C\rangle$ for the cases (a), (b), and (c) of Fig. 3.34 for a closed system where level $|C\rangle$ spontaneously decays to levels $|A\rangle$ and $|B\rangle$. The plot is for a very weak probe field, so only a tiny fraction of the population of level $|A\rangle$ leaves this state via interaction with the light. Figure courtesy S. M. Rochester.
FIG. 3.36 Same as in Fig. 3.35 but for an open system where state $|C\rangle$ spontaneously decays predominantly to states other than $|A\rangle$ and $|B\rangle$. Figure courtesy S. M. Rochester.